CHAPTER ONE: INTRODUCTION

1.1 Toner

Toner is a fine, polymer-based color powder which is used to form texts and images on the paper by electrophotographic technology. It is generally electrically charged or possesses magnetic properties. It is widely used in laser printers, photocopiers and fax machines, which are based on electrophotographic technology invented more than 30 years ago.

There are currently two types of toners manufactured by different processes: the chemically produced toner (CPT) and the conventional toner. Figure 1.1 below shows the scanning electron microscope (SEM) photograph of chemically produced toner and conventional toner[1]. The CPT is spherical, whereas the form of the conventional toner is irregular because it is pulverized mechanically. CPTs are smaller and have consistent particle sizes with narrower distribution than conventional toner. The common method in producing CPT is by emulsion aggregation process, in which a copolymer in latex form is first prepared by emulsion polymerization. This is followed by an emulsion aggregation of the latex with pigment, charge control agent and wax in the presence of coagulant to form toner particles of desirable sizes.

The conventional toner could be made from: (i) styrene-acrylate copolymer produced by radical initiated addition polymerization and (ii) polyester resin by stepwise condensation polymerization or (iii) combination of styrene-acrylate and polyester.

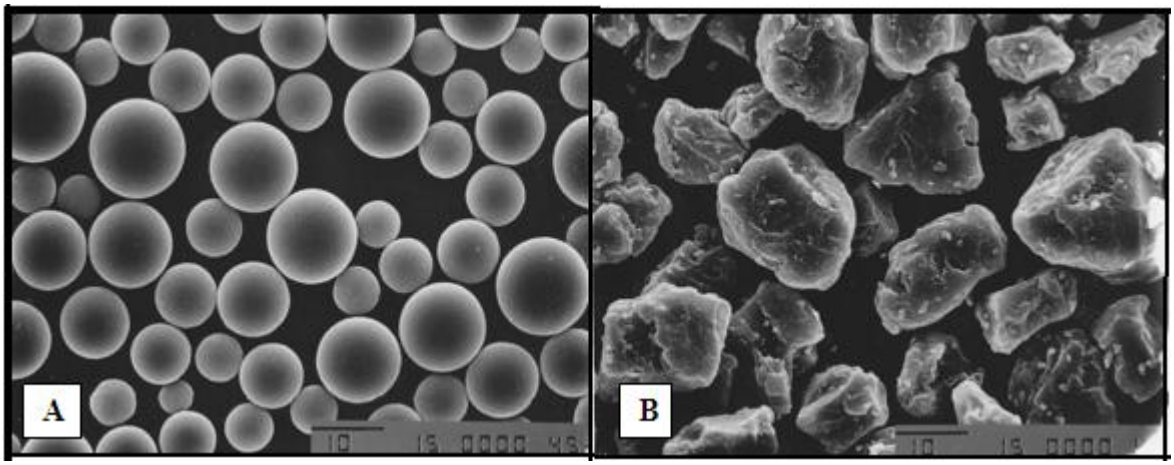


Figure 1.1 : SEM photograph of (a) chemically produced toner and (b) conventional toner[1]

The production volume of CPT in 2006 was around 6.7% of the total worldwide production volume of toners. This is an increase of 5.1% of the total worldwide production volume of toner from 2001. Although there is a growing trend in the development of CPT, the conventional toner is not expected to phase out in the near future as many major hardware manufacturers have lacked the core competency and facilities infrastructure to needed to conduct polymerization processes.

New advances in pulverization manufacturing techniques have led to conventional toner to be more efficiently produced with smaller and more consistent particle sizes. These new manufacturing techniques enable conventional toner to be more competitive against CPT. This study will be concentrating on conventional toner of styrene-acrylate copolymers.

1.2 Electrophotography

An electrophotographic process generally involves 5 steps which is imaging, inking, toner transfer, fusing or fixing and cleaning (as shown in Figure 1.2). Imaging is achieved by charging a photoconductive surface, usually a drum or a belt, with a uniform electrostatic charge by a corona or charge roller. The photoconductive surface charge is positive for most inorganic photoconductors and negative for organic photoconductors.[2]

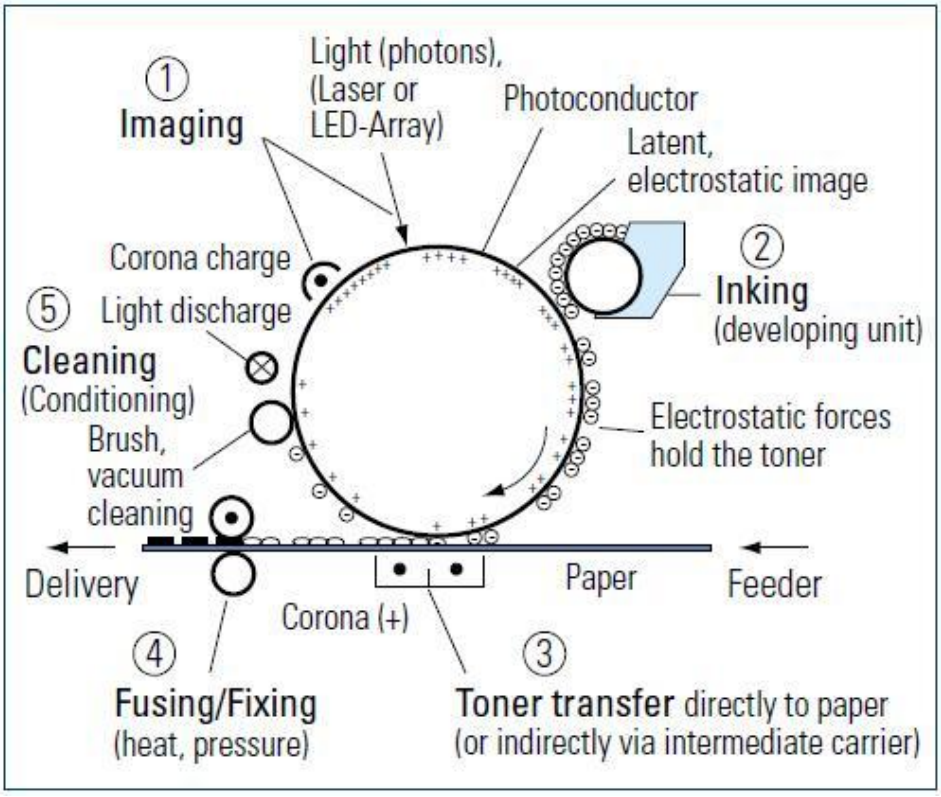


Figure 1.2: Basic principle of electrophotography[3]

The charged drum is then exposed to light to produce a latent electrostatic image on the photoconductor. The uniformed charge on the surface is partially discharged by the exposure. Inking takes place when the toner particles from the developer are transferred to the photoconductor through electric potential differences. The toner particles selectively adhere to the discharged area of the photoconductor, but repel from the charged area. After inking, the latent image becomes visible due to the toner applied.

The toner image can be transferred directly to the paper, but in some cases an intermediate carrier is used. This transfer is assisted by the contact pressure between the drum and the paper. The toner particles do not strongly adhere to the paper. Therefore, heat or pressure is used to permanently fix the toner particles to the paper.

Toner transferred from the photoconductor to the paper is not 100% efficient. Residual charges and individual toner particles can remain on the drum. To remove the remaining toner, a rotating brush is used and the toner falls into a waste sump. Finally, the residual latent image is erased by exposing it to light, and the photoconductor is prepared for the next image forming cycle.

1.3 Conventional toner Manufacturing Process

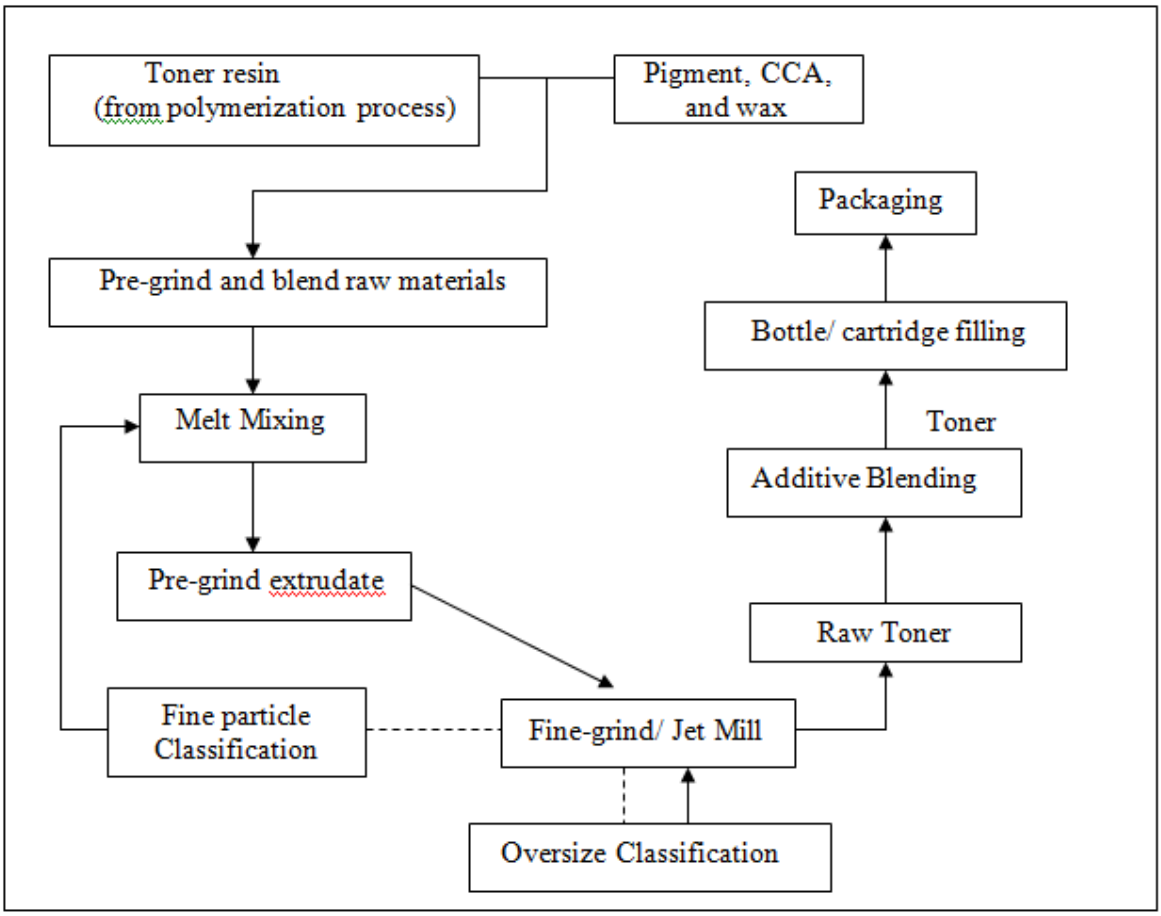


Figure 1.3: Diagram of the manufacturing process for conventional toner.

Figure 1.3 outlines the manufacturing process for conventional toner. First, toner resin prepared from the polymerization process is pre-mixed with pigment, charge control agent (CCA) and wax in a dry powder mixer. These are then fed into the preheated compounder and the mixtures are kneaded at a suitable temperature based on the melt flow index of the toner resin. The mixtures were extruded into sheet form and allowed to solidified by cooling.

The sheets were placed into a crusher and being crushed to coarse particles. It was followed by fine grinding using jet mill. After grinding, many particles that are significantly smaller or larger than desired will produced. Therefore, the particles are then subjected to a classifier to remove particles with undesired size. The larger particles that are rejected by classifier will recycle to the grinder and particles that below size specification to the melt-mixing stage.

Finally, the raw toner is subjected to addition of external additives by using blender at high blending speed to distribute additives uniformly over the surface of toner particles. After blending, the toner particles were sieved with a mechanical vibratory sieve of 100 μm to eliminate coarse particles. The toner is then filled into a cartridge and sends for packaging.[4]

1.4 Components of a toner

A toner comprises of a binder resin (toner resin), a colorant, a magnetic oxide, a charge control agent and other additives.

1.4.1 Binder Resins

The role of the resin is to bind and fix the toner onto the receiver, usually paper, thus creating a permanent image.[5] A resin is a polymeric material, and its characteristics are dependent on its composition. Molecular weight distribution of resin must be controlled to have an appropriate binding and releasing characteristic. A resin with bimodal molecular weight distribution is preferred. The low molecular weight fraction provides the fixing characteristics and the high molecular weight fraction prevent the offset phenomenon.

The resin is the main component of a toner and can make up anything between 45 to 95% of the toner.[6] The chosen resin must melt at a reasonable temperature as well as having desirable mechanical and tribo-electric properties.

The most common binder resins are polystyrene, styrene-acrylic copolymers, styrene-methacrylic copolymers, polyesters, epoxy resins, acrylics and urethanes. Styrene-acrylic copolymers have been most popularly used because of lower cost and the ease in adjusting molecular weight distribution and the control of tribo-electric charge. Polyester resin has high mechanical strength and superb viscoelasticity characteristics but it is more expensive than styrene-acrylic copolymers resin in general.[7]

1.4.2 Colorant

The colorants used in toners may be either dyes or pigments or a combination of both. Pigments are preferred because they display higher fastness to light and heat than dyes.[2] As for the black toner, carbon black is mainly used. Important properties of carbon black are their dispersibility in resin in hot melt mixing and their tendency to charge either positive or negative.[8]

Other than carbon black, magnetite is often used in toners to impart magnetic properties to the toner. Some charge control additives such as nigrosine are good black pigments, and their use in a toner can lead to reduction or elimination of the carbon black.

The content of the colorant in a toner formulation is not specifically limited, but has to be sufficient for coloring the toner, preferably set within a range from 3 to 15 parts by weight based on 100 parts of the total resins.[9] If the colorant used is carbon black, since the carbon black itself has conductivity, the amount of the colorant is set considering the electric characteristics of the toner.[9]

1.4.3 Magnetic Additives

The content of magnetite in a magnetic toner is usually in a range of 50 to 150 parts by weight based on 100 parts of the total resins.[9] It enables the transfer of the toner through the developer and against the latent image under magnetic control.

Besides, magnetic additives may also function as colorant.[10] Magnetic iron oxides are black or brown and therefore additional colorant is not required. Usually the magnetic additives are coated with chemical compounds to improve their dispersibility, to adjust tribo-electric properties of toner and to control humidity sensitivity of the toner.

1.4.4 Charge Control Agent (CCA)

Charge control agent is used to improve the charge transfer between the toner particles so that the charge distributions on the surface of the toner particles turn out to be relatively homogeneous.[11] It ensures that the toner particles acquire the correct level of tribo-electric charge and maintain stable charge over long periods of time. The presence of CCA produces sharper, higher density images, and decreased background.

Nigrosine is a commonly used CCA which is inexpensive yet effective in imparting a positive charge to the toner.[12] Due to its black color, it is suitable only for making black toner. Color toner would use other CCA which are either colorless or very light in color.

1.4.5 Other Additives

Small amount of one or more additives are usually added to adjust the performance of toner in various aspects, which include flow control, charge control, cleaning, conductivity control and decrease humidity sensitivity. Surface additives such as fumed silicas and titanias are added to the surface of the toner particles to improve flow characteristics and to prevent agglomeration. [5,12] The silica can also improve transfer from the photoreceptor to paper by lowering the adhesion of the toner to the photoreceptor surface while improving the charge stability of the toner and carrier mixture.[12]

For blade cleaning, zinc stearate is often used as lubricant to lubricate the blade passing over the photoreceptor. Release agent such as low molecular weight polyethylene or polypropylene wax is incorporated into toner to prevent toner adhesion to the fuser roller. The preferable wax melting point is about 50^{o}C to about 150^{o}C.[13]

1.5 Required Properties of toner

The principal requirement of any toner is to be able to provide a desirable output image on several media, which is usually but not always paper. So the design of a toner must take into account its interactions with all machine components, development system, photoreceptor, cleaning and fusing. In addition, the toner must be readily processable, stable to different environmental conditions, economical, odorless, non-irritating and pose no health risks.[12]

The typical styrene acrylic toner resins required the most important of these properties: (i) glass transition temperature, T_g, (ii) molecular weight distribution, (iii) melt viscosity, and (iv) particle size distribution.

1.5.1 Glass Transition Temperature, T_g

T_g is the temperature at which the polymer undergoes changes from a glassy state to a rubbery state. Blocking temperature of the toner, the temperature at which the toners transfer onto the paper is depending on the T_g of the toner resins. For adequate blocking, toners generally should have a T_g in the range of 50-65^oC.[14]

When T_g is lower than 50^oC, toner blocking or aggregation on a photoconductor of the printer occurs, thereby causing the problem that a dash mark is formed on the image. When T_g of the toner exceeds 65^oC, it becomes difficult to fix at a low temperature range.[9]

1.5.2 Molecular Weight Distribution

Commercial toner resins typically are polymer that has a broad polydispersity consisting of a mixture of a high molecular weight fraction and a low molecular weight fraction. Low molecular weight fraction would impart good fixing properties while the high molecular weight fraction could prevent the offset phenomenon that results from partial sticking of toner to the surface of hot roll.[15] When the toner is transferred to paper it is permanently fixed by the application of heat or pressure. This process is called fixing. On the other hand, offset is when the toner adhere to the fuser and being transferred readily to the paper.[12]

1.5.3 Melt Viscosity

Melt viscosity is measured by its melt flow index, which is a rating of the stiffness of the toner resins when heated to a given temperature and injected with a specific amount of pressure.[16] Melt viscosity should be in the range of 1 – 6 g/10 mins at 160^{o}C.[17] Desired range of melt viscosity needs to be achieved to obtain good fusing quality, and at the same time minimize offset and jamming issues.

1.5.4 Particle Size Distribution

Particles sizes of toner generally in the range from 7-12 µm, the smaller particle size would be effective in obtaining better image quality.[18] Particle sizes larger than 12 µm usually produce ragged lines and dots and thus degrade copy quality.

1.6 Print Defects in Laser Printers

Defects are often introduced into the images because of mechanical or material problems during imaging. Table 1.1 shows the classification of print quality defects. Few common print defects will be discussed in details.

Table 1.1: Classification of print quality defects

Group	Print Defects
Defects of uniformity	Banding, Streaks, Second side discharge marks
Random marks and repetitive artifact	Randomly scattered white specks, repetitive marks, repetitive lines, ghosting, leaked toner, tone bubbles, tone scatter
Color defects	Color plane registration, color consistency

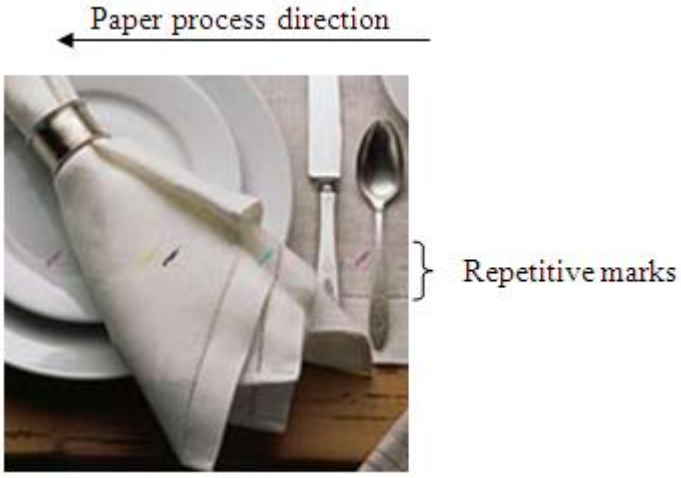
1.6.1 Banding

If banding occurs, the image appears to have lines or pinstripes in the direction of the print (as shown in Figure 1.4).[19] Banding can be random or periodic; it can be light or dark; it can be horizontal or vertical.

Figure 1.4: Image with banding defect

1.6.2 Repetitive Marks

Repetitive marks are due to localized contamination or damage occurring on the surface of a drum or roller. Normal imaging cannot take place at this point on the surface of the drum or roller and a localized artifact results because of the contamination or damage. With a multipass printer, the marks may appear in a sequence of different colors (as shown in Figure 1.5).



1.6.3 Ghosting

Printers that experiencing ghosting defects show repeated images of previously printed contents in the paper process direction. A positive ghost image occurs when it appearing on a printed sheet where it was not intended to appear, usually on white background. (as shown in Figure 1.6) A negative ghost image occurs when the printed image appearing too light on a black background. Ghosting is generally caused by the residual toner particles on the surface of an OPC drum or a fuser roll.[20,21] If a cleaning unit does not work properly, toner particles remaining from the previous image will be transferred onto the paper, thereby generating a ghost image.

Figure 1.6: Image with positive ghosting defects

1.7 Suspension Polymerization

Suspension polymerization is a polymerization process where the organic phase is dispersed as fine droplets throughout the water phase by continuous agitation, optionally in the presence of a colloid stabilizer. The initiator used is soluble in the monomer (organic) phase while the stabilizer is soluble in aqueous phase. Suspension polymerization generally produces bead particles with broad size distribution. Bead particles, with diameters in the range of 10 μm to 5 mm, are usually accompanied with unintended smaller particles.[22]

Suspension polymerization is similar to bulk polymerization, and it could be considered 'bulk polymerization within a droplet'. Figure 1.7 shows schematically the mechanism of formation of the bead particles. The bulk monomer is subjected to continuous mechanical agitation, which causes the elongation of the monomer into a threadlike form. Subsequently, the monomer breaks it into small a droplet that assumes a spherical shape under the influence of the interfacial tension. The individual droplet

undergoes continuous breakage and coalescence. A dynamic equilibrium is established when the sticky, viscous droplets transformed into rigid, spherical bead particles after the polymerization is completed.

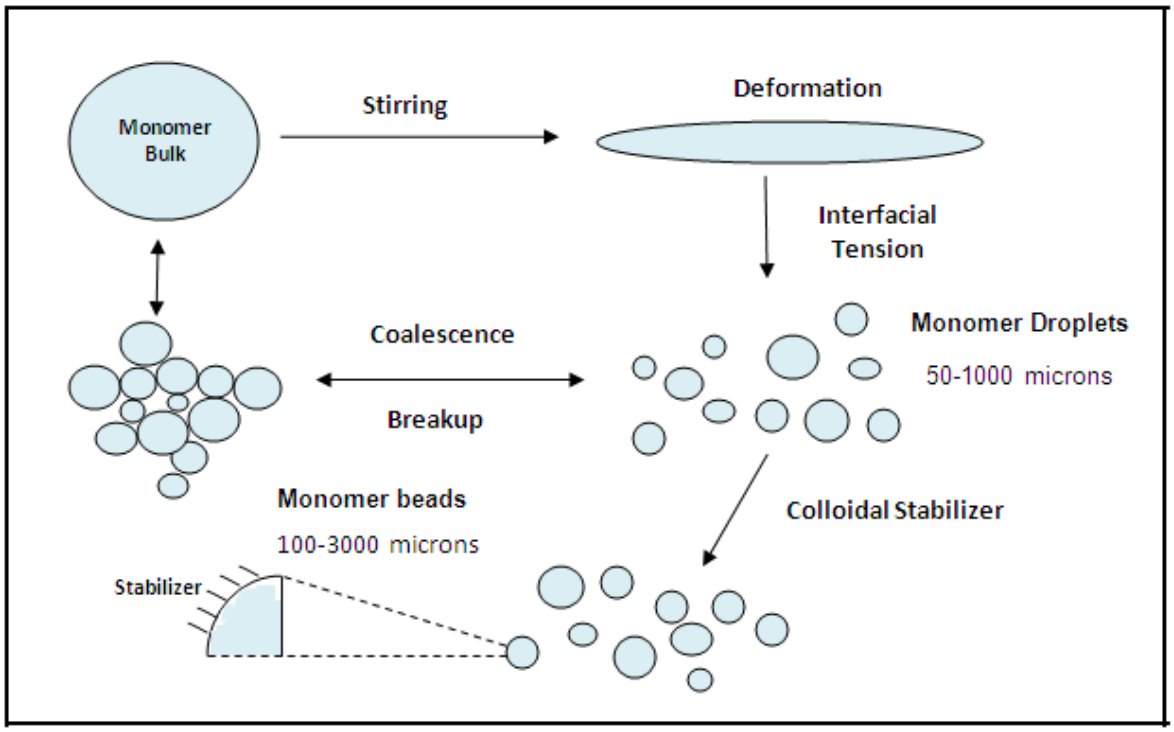


Figure 1.7: Schematic diagram of the stages of dispersion in suspension polymerization[23]

The particle size distribution, in principle, is determined by a balance between the breakage and coalescence rates. In regards with the breakage and coalescence phenomena, the suspension polymerization can be divided into three stages. In the first stage, when the viscosity of the dispersed phase remains low, droplet breakage is the dominant mechanism. During this stage, droplets sizes are changing constantly due to the shear stress imposed by the stirring conditions. Toward the end of this stage, average droplet size is almost constant.

When the viscosity of the dispersed phase reaches a critical value, due to the increasing conversion, the coalescence tends to overcome the breakage. Thus, the average particle size starts increasing. It is very important to control the coalescence behavior at this stage. Once the dispersion loses stability, the viscous droplets may agglomerate with the force of an avalanche and lead to the polymerization stopping. Normally, this phenomenon is prevented by suspension stabilizer, which absorbs at the monomer/water interface to enhance the stability of drops against coalescence.

The end of the second stage, also named the sticky stage, takes place when the viscosity of the dispersed phase reaches a second critical value. The coalescence is avoided; the particle growth is stopped due to the elastic nature of the particle collisions. The size of particles remains fixed and beads begin to appear hard. Thus, they cannot coalesce with each other and keep their identity for the remainder of the process. At that time, the polymerization only occurs within the fixed particles, and the dispersion system looks like a solid-liquid suspension. The function of the agitation then only lies in keeping the solid-liquid suspension and removing reaction heat.

The conditions of suspension polymerization could be controlled by: (i) monomer to water volume ratio, (ii) agitation speed, (iii) type and concentration of stabilizer, (iv) concentration of initiator, and (v) reaction temperature.

1.7.1 Monomer to water volume ratio

The volume fraction of the monomer phase to the water phase is usually within the range 0.1-0.5. [22] Polymerization reactions may be performed at lower monomer volume fractions, but are not usually economically viable. At higher volume fractions, the concentration of continuous phase may be insufficient to fill the space between droplets.[24]

1.7.2 Agitation speed

Increasing the agitation speed during the suspension polymerization has been found to lead to a decrease of the average particle size. This is due to higher breakage rate at the higher agitation speed. The average particle size is the result from the balance between breakage and coalescence processes. Therefore, the coalescence rate also increases resulting increase of the particle size. The net result is, however, increase of breakage rate that will outweigh the latter, thus producing a smaller particle.[25] Besides, the conversion, as well as the viscosity, at which the particle growth started, are not constant and could vary with the impeller speed.[22]

1.7.3 Type and concentration of stabilizer

The stabilizer reduces the interfacial tension between the monomer-polymer droplet and water, and it forms an interfacial layer around the monomer-polymer droplet surface to prevent coalescence. The performance of a stabilizer in terms of its stability to stabilize a droplet is determined by the molecular properties of the stabilizer. Their molecular properties may be represented by their molecular weight and degree of hydrolysis. Castellanos et al.[27] and Mendizabal et al.[28] had stated that the best poly(vinyl alcohol) for use as a stabilizer in suspension polymerization is the one with a degree hydrolysis of 80-90% and molecular weight of above 70,000 Dalton (1 Dalton = 1.66×10^{-27} kg).[22,26] The amount of stabilizer is preferably used in amount of ~0.1wt % of total dispersion solution.[23]

1.7.4 Concentration of initiator

The rate of polymerization increases with concentration of initiator increases. By increasing the concentration of initiator shorter polymer chains are produced and thus, reducing the molecular weight of polymer produced.

1.7.5 Reaction temperature

The rate of polymerization increases with temperature. A 10^{o}C temperature increase results in a two to threefold increase in the rate of polymerization. Therefore, the conversion increases with the same reaction time when the temperature is increased.

1.8 Free Radical Polymerization

A free radical polymerization mechanism includes initiation, propagation, and chain transfer to monomer, and termination. Free radicals must be introduced into the system to start the reaction. It usually produced by thermal decomposition of initiator (refer Figure 1.8). In this study, benzoyl peroxide was used as initiator.

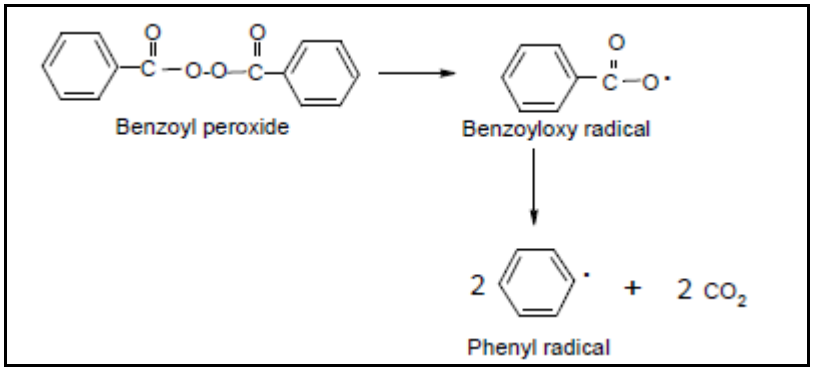


Figure 1.8: Thermal decomposition of benzoyl peroxide

Decomposition of benzoyl peroxide will give two identical radicals that can now attack the double bond of a monomer. In this case, radical initiator will react either with styrene or n-butyl acrylate. The reactions can be written as below.

$$R\cdot + M \longrightarrow M_x\cdot$$

where R· and M represent to radical initiator and monomer respectively.

Propagation then proceeds through the addition of monomer molecule to the growing chain, usually at fast rate.

$$M_x\cdot + M \longrightarrow M_{x+1}\cdot$$

Termination can occur via radical combination and chain disproportionation. Combination of two polymeric free radicals is the major terminating step for styrene polymerization.

$$M_x\cdot + M_y\cdot \longrightarrow M_{x+y}\cdot$$

Disproportionation occurs during the radical collision if hydrogen atom is transferred from one radical chain to the other. This also leads to the loss of two reactive radical sites and its equivalent to a termination reaction.

$$M_x\cdot + M_y\cdot \longrightarrow M_x + M_y$$

In free radical polymerization, there is the possibility of chain transfer reactions, where a growing chain radical is terminated and a new one is initiated. Such reactions can occur between the radical site with another polymer, monomer or solvent molecule.

$$M_x\cdot + R\text{—}H \longrightarrow M_x + R\cdot$$

$$R\cdot + M \longrightarrow R\text{—}M\cdot$$

1.9 Gel Effect

Cross-linking is accompanied by the formation of gel at some point of the polymerization. The cross-linking reaction is not very fast and chains can grow in more than two directions at the cross-linking point by the addition of monomers. Three types of polymer configurations are produced which are linear portion, sol and gel.[29]

Linear portion is a soluble portion and the cross-linked portion which is low in cross-linking density and therefore, is soluble in some solvents like tetrahydrofuran is referred to as sol. The gel is insoluble in all solvents at elevated temperatures under conditions where polymer degradation does not occur. The gel corresponds to the formation of a 3-D network in which the polymer molecules have been cross-linked to each other to form a macroscopic molecule.

As the polymerization and gelation proceed beyond the gel point, the amount of gel increases at the expense of the sol as more and more polymer chains in the sol are cross-linked to the gel.

1.10 Selection of Monomers

The role of the resin in a toner is to bind the pigment to the paper to form a permanent image. This is typically done by selecting a polymer that will melt at reasonable temperature when heat is applied.[8] The resin used in this study is styrene acrylic copolymers which are usually used in both negative as well as positive charge toners.

Around 90% or more of the toner is polymer; its cost is very important in determining the cost of the final product. Based on this consideration, styrene is low in cost and became increasing available in recent years. Styrene copolymerized with acrylic acid provides superior hardness and abrasion resistance.[30] Unlike some other monomers, styrene

is a liquid that has a low vapor pressure at ambient conditions, making it easy to ship, handle and store.[31]

N-butyl acrylate is commercially important in the synthesis of acrylic resins because of their optical clarity, mechanical properties, adhesion and chemical stability.

1.11 Scope of Study

The objective of this study is to produce styrene acrylic copolymer resins with the required properties of toner resin for industrial application by using suspension polymerization process. A typical toner resin has a bimodal molecular weight distribution, which shows that it contains one fraction of lower molecular weight and another fraction of higher molecular weight, so that it can impart good fixing and offset properties to meet the requirements of a good toner.

The first chapter contains brief introduction of electrophotographic process, the introduction on toner and its required properties, suspension polymerization method and common print defects in laser printers. Chapter two describes the synthesis of styrene acrylic copolymers which includes the experimental works in the preparation and characterizations. The preparation of toner by using pilot plant facilities is also described in this chapter.

Chapter three contains results relevant to the experimental and characterization works done in Chapter two. Comparison between synthesized toner and commercial toner and evaluations of printing test were also discussed in this chapter. Chapter 4 includes a summary and some suggestions for future works.

CHAPTER TWO: EXPERIMENTAL

2.1 Synthesis of Styrene Acrylic Copolymers

2.1.1 Materials

Styrene, n-butyl acrylate and acrylic acid were technical grade chemicals from Sigma-Aldrich. They were used as received. The initiator, benzoyl peroxide (containing 25% H_2O), was analytical grade reagent and also from Sigma-Aldrich. The colloid stabilizer was poly(vinyl alcohol) (PVOH) with average molecular weight M_n of 88000 Dalton (1 Dalton = 1.66 x 10^{-27} kg) was from Fisher Scientific (M) Sdn. Bhd. The continuous phase was distilled water. The cross-linking agent (CLA) used was tetra(ethylene glycol) diacrylate supplied by Sigma-Aldrich.

2.1.2 Apparatus

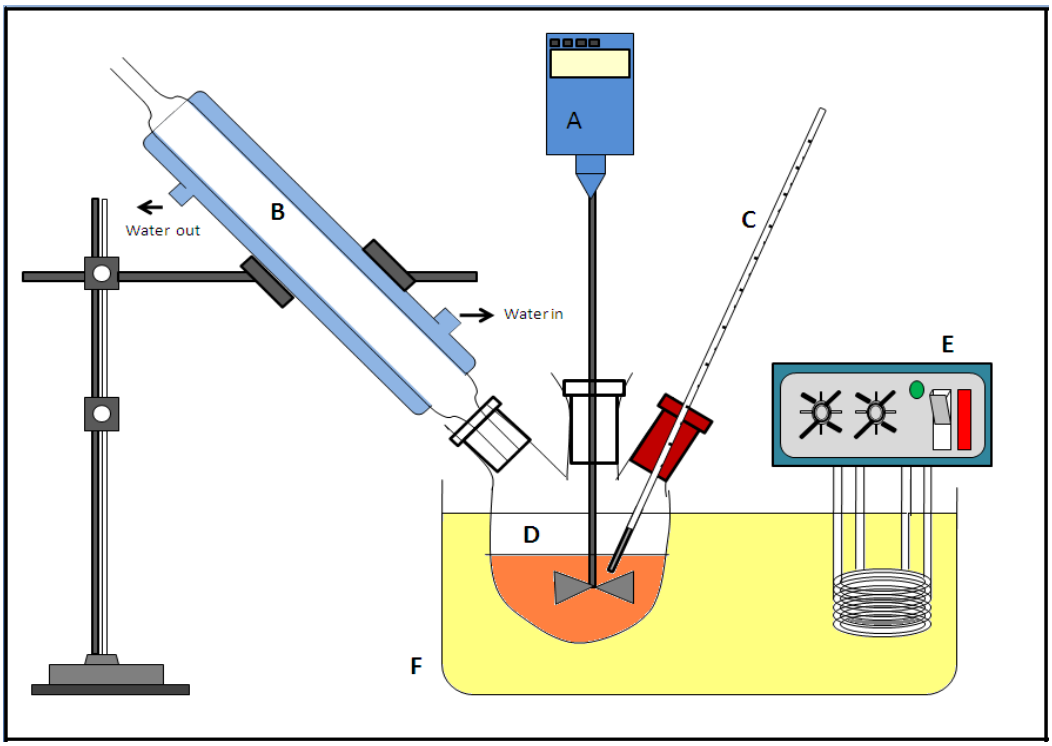


Figure 2.1: Apparatus for synthesis Styrene Acrylic Copolymer (A: mechanical stirrer, B: condenser, C: thermometer, D: reactor flask with detachable lid, E: heater controller, F: water bath)

2.1.3 Suspension polymerization

A 750 ml five-necked round bottom glass reactor flask equipped with a condenser, a thermometer, and a mechanical stirrer was used. A picture of the reactor setup was shown in Figure 2.1. The aqueous medium was prepared by dissolving 0.13 g of poly(vinyl alcohol) in 125 ml of distilled water and introduced into the reactor first.

The required amounts of monomers and initiator were mixed in a beaker and bubbled with nitrogen gas to remove dissolved oxygen. The monomer mixture was then added into the reactor. At this juncture, the reactor was cooled by an ice bath to avoid the polymerization from starting before a stable suspension was achieved. The mixture was then mechanically stirred at 400 rpm to produce suspension of fine droplets.

The ice bath was replaced with a water bath with the water preheated to 80-85^{o}C. Polymerization was carried out for 6 hours. (The stirrer may not be stopped as the polymerization proceeds until the time that the polymer beads have hardened; otherwise the tacky suspension particles could coalesce to form a big lumpy mass.)

The reactor was then allowed to cool down to room temperature before the copolymer beads were isolated by filtration and washed several times with distilled water to remove the water-soluble poly(vinyl alcohol) which has served as the colloid stabilizer. The beads were dried in an oven overnight at 45^{o}C. Copolymers of different molecular weights were obtained by varying the formulations.

2.2 Formulations

2.2.1 Low Molecular Weight Styrene Acrylic Copolymer

Two series of experiments to produce low molecular weight styrene acrylic copolymer by varying the monomer ratio and concentration of initiator were investigated. The formulation of low molecular weight toner resins is shown at Tables 2.1 and 2.2. The resulting copolymers were characterized. The one that has the suitable properties (to be discussed in Chapter 3) was chosen for blending with a high molecular weight copolymer for making of toner.

Table 2.1: Series 1 - Different monomer ratios at constant initiator concentration

Sample Code	**L20-RT**	**L21-RT**	**L22-RT**	**L15-RT**	**L16-RT**
Formulations/ Parts per 100 parts of monomers by weight					
Styrene	75	80	85	90	95
BA	25	20	15	10	5
Benzoyl Peroxide	15	15	15	15	15
Total	115	115	115	115	115

Table 2.2: Series 2 – Different concentrations of initiator at constant monomer ratio

Sample Code	**L23-RT**	**L24-RT**	**L25-RT**	**L18-RT**	**L16-RT**
Formulations/ Parts per 100 parts of monomers by weight					
Styrene	95	95	95	95	95
BA	5	5	5	5	5
Benzoyl Peroxide	5.0	7.5	10.0	12.5	15.0
Total	115	115	115	115	115

2.2.2 High Molecular Weight Styrene Acrylic Copolymer

Two series of experiments to produce high molecular weight styrene acrylic copolymer by varying the monomer ratio and concentration of cross-linking agent were investigated. The formulation of high molecular weight toner resins is shown at Tables 2.3 and 2.4. The resulting copolymers were characterized. The one that has the suitable properties (to be discussed in Chapter 3) was chosen for blending with a low molecular weight copolymer for making of toner.

Table 2.3: Series 3 – Different monomer ratios at constant AA, initiator and CLA concentration

Sample Code	**H22-RT**	**H15-RT**	**H16-RT**	**H17-RT**	**H23-RT**
Formulations/ Parts per 100 parts of total monomers by weight					
Styrene	70	75	80	85	90
BA	30	23	18	13	8
AA	2	2	2	2	2
Benzoyl Peroxide	1	1	1	1	1
CLA	0.1	0.1	0.1	0.1	0.1

CLA = tetra(ethylene glycol) diacrylate

Major monomers: styrene and butyl acrylate

Table 2.4: Series 4 – Different concentrations of cross-linking agent (CLA) at constant monomer ratio and initiator concentration

Sample Code	**H17-RT**	**H18-RT**	**H19-RT**	**H20-RT**	**H21-RT**
Formulations/ Parts per 100 parts of total monomers by weight					
Styrene	85	85	85	85	85
BA	13	13	13	13	13
AA	2	2	2	2	2
Benzoyl Peroxide	1	1	1	1	1
CLA	0.1	0.2	0.3	0.4	0.5

2.3 Mixing of High Molecular Weight and Low Molecular Weight Styrene Acrylic Copolymer

One low molecular weight copolymer (LMW) and one high molecular weight copolymer (HMW) were identified from the series described in section 2.2.1 and section 2.2.2. The one that has the suitable properties (to be discussed in Chapter 3.3) was chosen to blend at different ratios (LMW/HMW, 50/50, 40/60, 30/70, 20/80, 10/90). 10.0 g of blended copolymer was mixed with 20.0 ml of toluene. The mixture was allowed to stand overnight for dissolution to occur. Then, the blended copolymer was precipitated out by adding methanol. The precipitated copolymer was spread on a glass plate and dried in an oven at 100^{o}C for overnight. The resultant copolymer was collected and used to run the series of properties tests.

2.4 Preparation of raw toner by using Pilot Plant

2.4.1 Materials

Mixed resins (as described in section 2.3), magnetite pigment, charge control agent (CCA), and wax.

2.4.2 Procedures

The pilot plant consists of Henschel mixer, kneading machine, crusher, jet mill, and classifier. The raw toner was prepared by a process consisting of premixing, kneading, crushing, milling, and classification. The sequence of the process is shown in Figure 2.2. For a laboratory scale production of the toner, a total of 3.0 kg of materials consisting the blended resin, magnetite pigment, charge control agent and wax was fed into a Henschel mixer surrounding by outer cooling water jacket (Appendix A- Figure A.1). Then, the mixture was subjected to high rotational speed for 1 minute each at 600 rpm, 800 rpm and 1000 rpm.

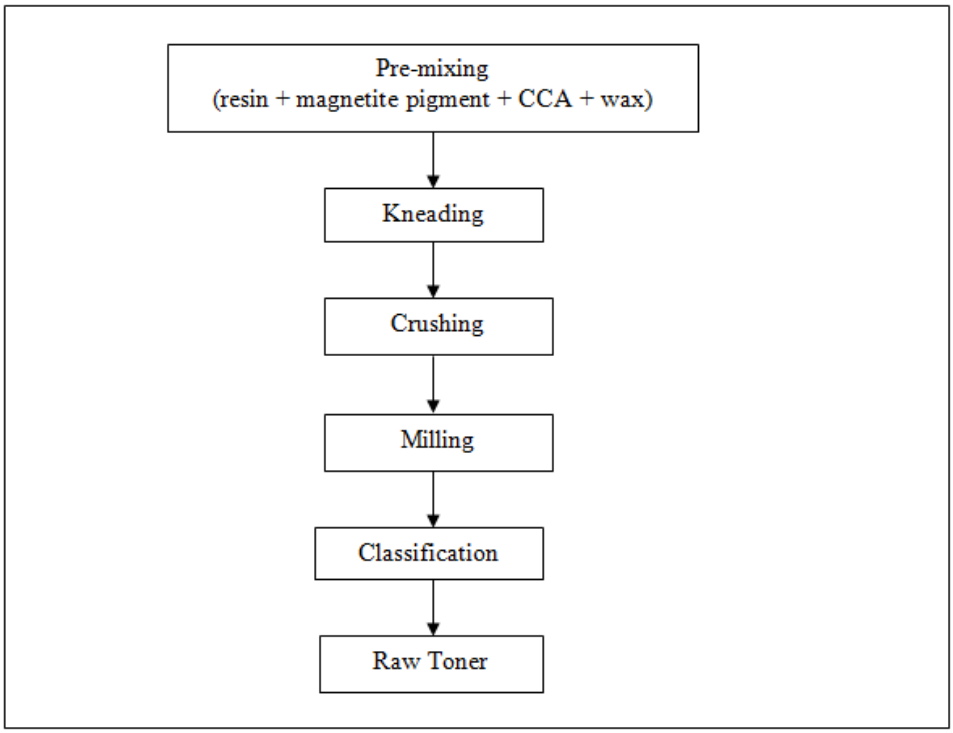


Figure 2.2: Process to produce raw toner

After pre-mixing, the mixture is transferred into a kneading machine or extruder. The extruder has the dual purpose of mixing and heating the mixture into a homogeneous polymer melt at a suitable temperature based on the melt flow index of the blended resin. The melt is then extruded into sheet form and allowed to solidify by cooling. The sheets were placed into a crusher and being crushed to coarse particles. Coarse particles were sent through a milling process by using jet mill to reduce its particles size. Typically, milled particles have a broad size distribution. To achieve narrow size distribution, milled particles were subjected to a classification step. Finally, raw toner with desired particle size distribution is produced.

2.4.3 Formulation

The formulation to produce raw toner by using pilot plant is shown in Table 2.5.

Table 2.5: Formulation to produce raw toner

Materials	**Amount/ %**	**Weight/g**
Blended resin	54.5	1635.0
Magnetite pigment	44.0	1320.0
Charge control agent	0.5	15.0
wax	1.0	30.0
Total	100.0	3000.0

2.5 Preparation of toner

2.5.1 Materials

Raw toner (as described in subsection 2.4), magnetite pigment, silica and surface additive.

2.5.2 Procedures

Raw toner was blended with magnetite pigment, silica and surface additive to produce toner by using blender. Around 306 gram of this mixture was subjected to high blending speed for 4 minutes. After blending, the toner particles were sieved with a mechanical vibratory sieve of 100 μm to eliminate coarse particles.

2.5.3 Formulation

Final blending formulation to produce toner is shown in Table 2.6.

Table 2.6: Formulation to produce toner

Materials	**Amount/ %**	**Weight/ g**
Raw toner	98.00	300.00
Magnetite pigment	0.98	3.00
Silica	0.98	3.00
Surface additive	0.04	0.12
Total	100.00	306.12

2.6 Evaluation of Print Quality

The toner was filled into a toner cartridge and a series of print test was carried out according to ISO-IEC 19752 monochrome print test protocol. Twelve plain paper sheets were printed with the same toner. Each sheet consisted of different test image include different percentage of halftones, A to Z characters, black page, gray (25% halftone) page, and lines of varying widths designed to evaluate print quality (as shown in Figure 2.3). Besides, another print test was carried out using commercial toner in a similar manner as that of the synthesized toner to compare the print qualities.

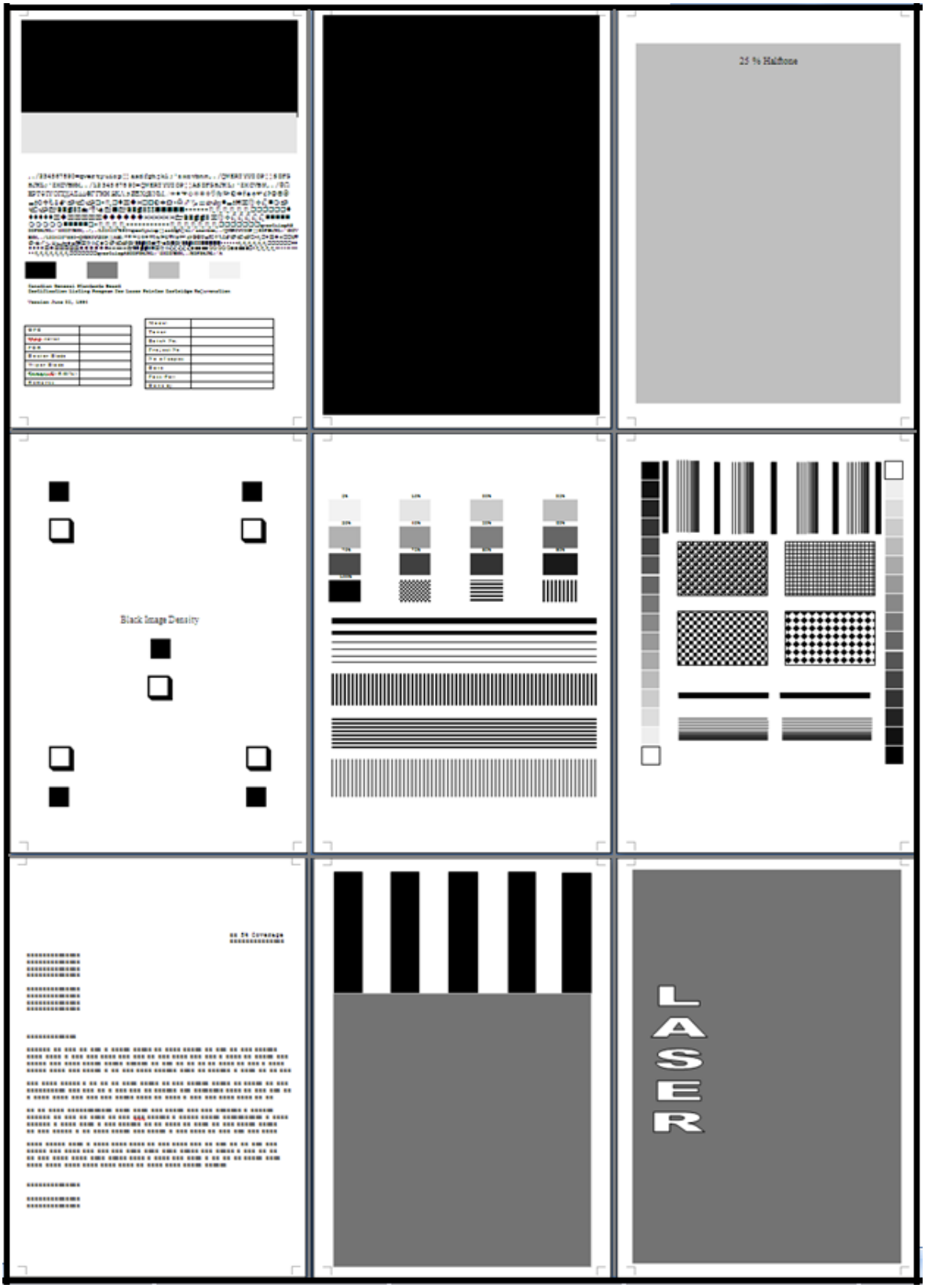


Figure 2.3: Test images

2.7 Characterization of toner resins and toners

2.7.1 Determination of Glass Transition Temperature, T_g

T_g is the temperature at which the polymer undergoes changes from a glassy state to an elastomeric state. T_g of the toner resin was measured using a Mettler Toledo differential scanning calorimeter 822^e. Before beginning measurement, the DSC was calibrated with indium standard. Around 10-11 mg of the toner resin or toner was weighed using an aluminum pan and another empty aluminum pan as reference. Measurements on samples were carried out over a temperature range of 30-100^oC at a heating rate of 10^oC/min under a nitrogen atmosphere. Likewise, the second scan was recorded under the same condition. The first scan of the DSC represents the thermal history of the sample. Therefore, the T_g was based on the result of the second scan. The T_g was determined as the midpoint of the endothermic displacement between linear baselines (Appendix C).

2.7.2 Determination of Molecular Weight Distribution

Molecular weight distribution and polydispersity index were obtained by gel permeation chromatography system consisting of a Water 1515 Isocratic HPLC Pumps and Water 2414 Refractive Index Detector and three Styragel HR series columns. This instrument was calibrated with monodisperse polystyrene standards with known molecular weights.

0.05 g of toner resin or toner was mixed with 5 ml of THF and allowed to stand overnight for complete dissolution of soluble fraction to occur. The mixture was then filtered by Minisart NY 0.45 μm single filter. 20.0 μl of the sample solution was injected manually into the column. The run time of the analysis was 36 minutes.

2.7.3 Infrared IR Spectrum

0.1 g of toner resin was mixed with 5 ml of toluene and allowed to stand overnight for complete dissolution at room temperature. IR spectrum was obtained using cast film method. A drop of resin solution was deposited on the surface of sodium chloride cell. The solution was then evaporated to dryness and the film on the cell was analyzed using Perkin-Elmer spectrum RX1 FTIR spectrophotometer. The spectrum was scanned for four times with the range of 500-4000 cm^{-1} and resolution of 2.0 cm^{-1}.

2.7.4 Percentage of Conversion

Monomer conversion in the suspension polymerization process was measured gravimetrically. A sample of the copolymer beads were filtered from the suspension and dried in the vacuum oven at 45^{o}C for 4 hours to drive off the water. The monomer conversion was calculated using the following equation.

$$\text{Percentage of Conversion} = \frac{\text{Weight of dried copolymer beads}}{\text{Initial monomer content in the suspension}} \times 100\%$$

2.7.5 Percentage of Tetrahydrofuran (THF) Insoluble Fraction

About 1.0 g of toner resin is weighed (w) and mixed with 50 ml of THF. The mixture was allowed to stand at room temperature for 24 hours. The weight of a filter paper was weighed and recorded as w_0. Then, the mixture was filtered through the filter paper and the insoluble fraction would be retained in the filter paper as residue. The filter paper with its content was dry in an oven at 100^{o}C for 4 hours. The filter paper was weighed again and recorded as w_1. The percentage of THF insoluble fraction can be obtained by using the following equation:

$$\% \text{ THF Insoluble Fraction} = \frac{\text{Residue weight}}{\text{Sample weight}} \times 100\% = \frac{(w_1 - w_0)}{w} \times 100\%$$

2.7.6 Melt Flow Index

The melt flow index (MFI) is defined as the weight of the toner resin or toner (in grams) extruded in 10.0 minutes through a capillary of specific diameter and length at the specific pressure applied through dead weight under prescribed temperature condition.[32] This test indicates the flow characteristics of polymer. MFI was determined by using a Ray-ran Melt Flow Indexer.

The apparatus and die were cleaned with thinner before use. If it is not clean, it can significantly influence the flow rate results. The stable test temperature was set with the temperature controller. Small die was inserted into the extruder. Around 5.0 to 10.0 g of toner resin or toner was inserting into the extruder and packed properly to avoid formation of air pockets. Next, the piston was inserted which acts as the medium that causes extrusion

of the molten polymer. The sample is preheated for 360.0 seconds at 120^{o}C, 150^{o}C and 160^{o}C for low molecular weight toner resin, high molecular weight toner resin and toner respectively. After the preheating, a specified weight load is introduced onto the piston. On account of the weight shear is exerted on the molten polymer and it immediately starts flowing through the die. For all tests, a timed extrudate is weighed accurately. The remainder of the samples was discharged through the top of the cylinder. Again, the apparatus and die were clean with thinner for next testing.

The MFI could be calculated through the followed equation.

$$\text{MFI} = \frac{w}{t} \times 600$$

Where,

w = weight of sample flown through, g

t = time for sample flow, s

2.7.7 Determination of Acid Number

The acid number (AN) is the number of milligrams of potassium hydroxide (KOH) required neutralizing the alkali-reactive groups in 1.0 g of toner resin. The acid number was determined experimentally for every sample of toner resin by titration.

First, standardization of KOH need to be carried out by determined the actual normality of KOH. It is determined by dissolving about 0.50 g of potassium hydrogen phthalate (KHP) in 50.0 ml of distilled water and the solution is titrated with 0.10 N of KOH in ethanol with phenolphthalein as indicator until the first appearance of pink color that persists for 30 seconds. The volume of KOH used was recorded. The procedure was

repeated for three times to get the average values. The actual normality of KOH can be calculated through the following equation:

$$N = \frac{(1000 \times w_{KHP})}{(204.23 \times V_{eq})}$$

Where, N = Normality of standardized KOH solution

W_{KHP} = Weight of KHP used, g

V_{eq} = Volume of KOH used for the sample titration, ml

204.23 = equivalent weight of KHP

Blank titration was carried out on the solvent. 50.0 ml of toluene is titrated with 0.10 N standardized KOH solutions with phenolphthalein as indicator. Titration was repeated for three times to get the average values and volume of KOH used was recorded as V_{blank}.

About 1.0 g of toner resin was weight accurately and dissolved in 50.0 ml of toluene by using a 250 ml of conical flask. Add few drops of phenolphthalein and titrate with KOH solution until the first appearance of pink color that persists for 30 seconds. Titration was repeated for three times to get the average values volume of KOH used was recorded as V. The acid number can be calculated by using the following equation:

$$AN = \frac{56.1 \times N \times (V - V_{blank})}{W}$$

Where, N = Normality of standardized KOH solution

V = Volume of KOH used for the sample titration, ml

V_{blank} = Volume of KOH used for the blank titration, ml

W = weight of sample used, g

56.1 = equivalent weight of KOH

2.7.8 Tribo-charge

The method of charge characterization on toner is the measurement of the charge-to-mass ratio. The toner charge-to-mass ratio determines the amount of toner developed and toner with the wrong sign charge is known to degrade image quality in the printing performance. The ratio of difference between charge and mass is called tribo-charge. Tribo-charge is determined using the "Blow-off" method.

The testing was done in accordance to ASTM F1425.[33] The empty sample cell which contains very fine screen (400 meshes) was weighed. Around 0.10 g of the test toner and 2.00 g of carrier were weighed and transferred into the sample cell. The mixture of toner and carrier is called developer. The sample cell which contains developer was manually shaken for 1 minute to generate charge between toner and carrier.

The sample cell is held by the tribometer which provides an electrical connection between the sample cell and the electrometer. An air flow was blown through the sample cell, separating toner particles from the carrier particles by filtration of the fine meshes. The separation process produced net charges in the sample cell and the toner charge was measured by the electrometer. When the test was completed, the electrometer reading was recorded and the tribo-charge of the test toner is calculated by using the following equation:

$$\text{Tribo-charge} = \frac{\text{- Electrometer reading}}{10 \times \text{weight of the toner}} = \mu C\, g^{-1}$$

2.7.9 Apparent Density

Apparent density is defined as the weight per unit apparent volume of a material, including voids inherent in the material as tested. It provides a measure of the fluffiness of a material. Apparent density is measured with the apparatus as shown in Appendix B (Figure B.5).

Test is performed by pouring the test toners through a funnel onto a conveyor belt and allowing the toner powder to fall through flowmeter funnel into a density cup with known volume. When the powder completely fills the density cup, excess powder will then be scraped off with a straight-edged bar without shaking the cup. The apparent density of the test toner is calculated by using the following equation:

$$\text{Apparent Density} = \frac{W}{V}$$

Where, W = weight of the test toner in the cylinder, g

V = volume of density cup, cm^3

2.7.10 Flowability

The flow characteristic of toner is determined by using the Flotest Tester. The determination of flowability is based upon the ability of toner powder to fall freely through a hole in the disc. The smaller the hole through which the powder falls freely, the better is the flowability.

Around 50.0 g of the toner powder was loaded into cylindrical container by using the funnel. After loading, toner was settled down for 10 seconds then release lever was adjusted to open the hole of flow disc. Flowability of toner powder was observed to check whether toner will flow out from the flow disc and leave a visible hole. If the toner did flow, the same procedure was repeated with smaller flow disc until results was negative. The

diameter of the smallest hole the toner powder that fell through freely on three successive attempts was recorded as flowability index.

2.7.11 Particle Size Distribution

Particle size distribution of toner is determined by using CILAS 1064 particle size analyzer. 0.50 g of toner powder was dispersed into 50.0 ml of dilute common detergent. The dispersion was then poured into the particulate dispersion device and particle size distribution of toner particles was measured by laser diffraction method.

2.7.12 Magnetic Content

The magnetic content of the toner is determined by using Tectron Ag. 916 Fluxmeter. The changes in the magnetic flux density of a magnetic coil due to insertion of the toner sample will be measured. Before any measurements, calibration of magnetic coil should be done with a standard demagnetized sample which will give a value of 1.04. The fluxmeter control then should be reset to zero. Around 1.50 g of test toner was filled into a test tube, and then inserted into the magnetic coil of fluxmeter. Three measurements were carried out and average value was calculated.

2.7.13 Image Density (ID) and Background Density (BD)

Image density and background density were measured by using QUIKDens 100 Densitometer. Image density evaluations were made on the one inch solid area blocks at different locations within the test print page. While background density evaluations were made on the open areas of the one inch square hollow blocks. The measurements were done by virtually place the aperture (3 mm) of densitometer on the target area and the values will appear. Five values were taken and average value was calculated.

CHAPTER THREE: RESULTS AND DISCUSSION

3.1 Synthesis of Low Molecular Weight Styrene Acrylic Copolymer

3.1.1 Series 1: Different monomer ratios at constant initiator concentration

The effect of different weight ratios of styrene: butyl acrylate was studied using the formulation shown in Table 3.1. Monomer composition (Sty/BA = 75/25, 80/20, 85/15, 90/10, 95/5) was varied to obtain copolymer that has T_g within the range of 50-65^oC that was suitable for making toner[14]. The DSC curve of the low molecular weight resin gradually shifts to the right as the styrene content increased as shown in Figure 3.1. Extrapolation of T_g refer to Appendix C (Figure C.1-C.5).

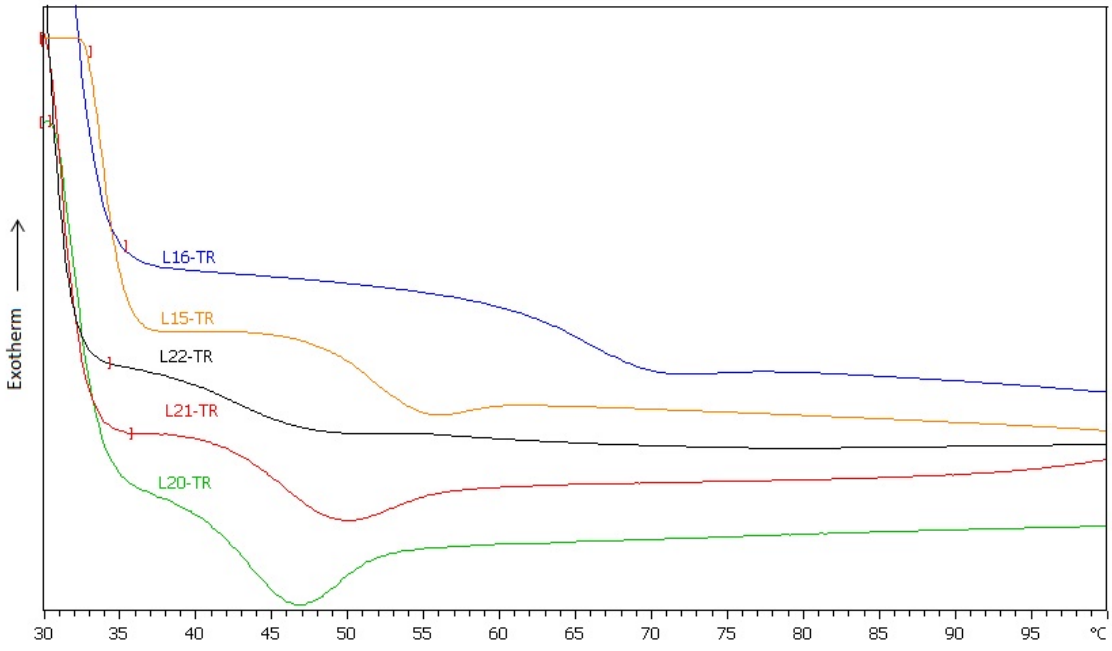


Figure 3.1: DSC thermogram of L20-TR, L21-TR, L22-TR, L15-TR and L16-TR at the heating rate of 10^oC/min

Polystyrene has a T_g of 373 K (100°C) while poly(butyl acrylate) of 218 K (-55°C).[34] The Fox equation has been used to estimate the T_g of copolymer by assuming the dependence of T_g on composition for a copolymer as:[35]

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

Another equation in use is Gordon-Taylor equation:[36]

$$T_g = \frac{(w_1 T_{g1} + k w_2 T_{g2})}{(w_1 + k w_2)}$$

T_{g1} and T_{g2} are the T_g's of the poly(butyl acrylate) and polystyrene and w_1 and w_2 are their respective weight fractions in the mixture. A value 0.3445 was used for k (refer appendix I), which was treated as a fitting factor. The experimental and calculated T_g according to Fox equation and Gordon-Taylor equation (k=0.3445) are shown in Figure 3.2, as a function of composition of the styrene. T_gs of the copolymers from 75-95 parts of styrene estimated by using Fox equation range from 316 K to 360 K and those T_gs measured by DSC were in the range of 312 K to 335 K. The T_gs of the copolymers are in the similar increasing trend with increasing styrene content as predicted by both equations. In general the T_g estimated from Fox equation is higher, while that from Gordon-Taylor equation is lower than the experimentally measured T_g. This is expected, as both the equations are more applicable to polymer blends of two components that are miscible or with strong interaction. In this case, the random distribution of styrene and BA unit in this copolymer and the specific interactions between the different segments of copolymer chain may lead to non-linear effects. However, Fox and Gordon-Taylor equations do not take these into considerations. Thus the fit to the equation would not be very good.

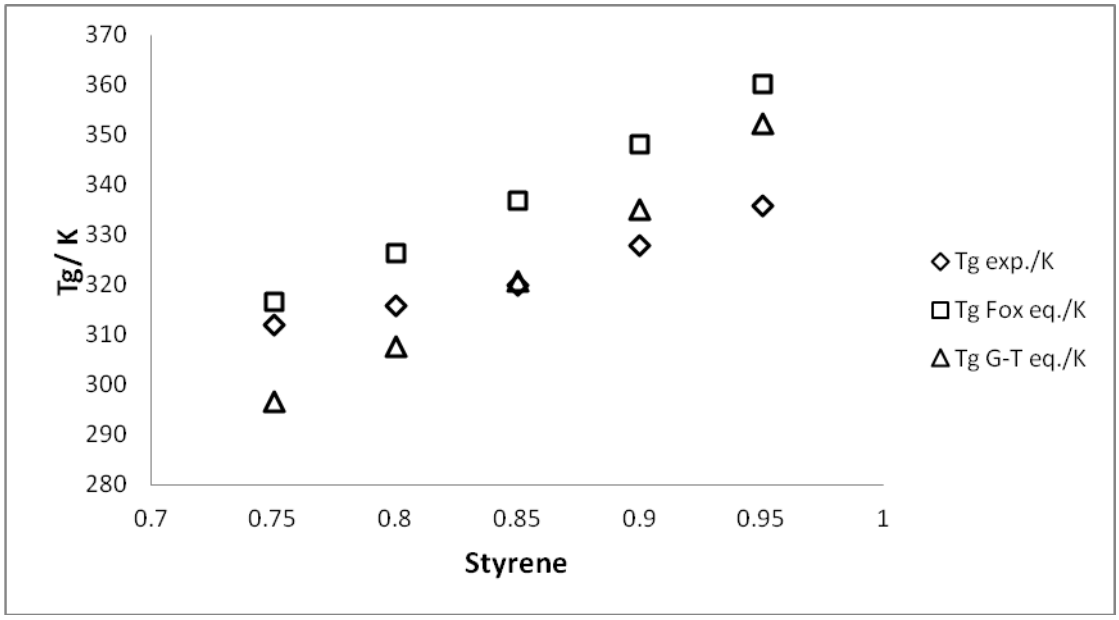


Figure 3.2: Comparison of T_gs of Styrene Acrylic Copolymers obtained from experimental and calculation by Fox equation and Gordon-Taylor equation (k=0.3445)

The FT-IR spectra of styrene-acrylate copolymers with different monomer compositions are presented in Figure 3.3. As can be seen, aromatic ring of the styrene units has given rise to C=C in-plane stretching vibrations at 1493 and 1601 cm^{-1} and C-H aromatic stretching vibrations at 3100-3026 cm^{-1}.[37,38] The absorption bands at 698 and 758 cm^{-1} are assigned to the aromatic CH deformation of the benzene ring, whereas those at 2924-2852 cm^{-1} are attributed to the aliphatic C-H stretching vibrations.[39] While the intense absorption peak at 1724 cm^{-1}, attributed to stretching vibration of C=O is from butyl acrylate.[37]

The monomer composition in the copolymer could be reflected by the spectral peak ratio of C-C to C=O bands in the FT-IR spectra. Styrene-acrylate copolymer contains several spectral bands which are mutually exclusive to one co-monomer, with little or no contribution by the other co-monomer. The 1724 cm^{-1} band is due to the C=O stretching of carbonyl group of n-butyl acrylate.[37] Band at 1601 cm^{-1} is attributable to the breathing mode of the aromatic ring of styrene units.[37,38] Ratios of the peak absorbance 1601 cm^{-1}/1724 cm^{-1} represent the relative amounts of constituents of the copolymer.

Table 3.1: FT-IR spectral peak area ratio of 1601 cm^{-1}/1724 cm^{-1} bands in the Styrene Acrylic Copolymers

Sample	**Ratio of Sty/BA used**	**A_{1601}**	**A_{1724}**	**A_{1601} / A_{1724}**
L20-TR	75/25	0.03	0.16	0.19
L22-TR	85/15	0.03	0.13	0.23
L16-TR	95/5	0.08	0.15	0.53

From Table 3.1, **A_{1601} / A_{1724}** ratio increase from 0.19 to 0.53 as the proportion of styrene in the copolymer is increased.

This series of samples was targeted to produce a low molecular weight resin to provide the fixing properties of toner by adding high amount of benzoyl peroxide as initiator into the system. Polydispersities are in the range of 1.8 to 2.1 (Table 3.2).

Melt flow indices of these low molecular copolymers are in the range of 13.0 to 77.0 g/10min at 120^{o}C. The melt flow index of the resins increases as the molecular weight decreases. As for sample L20-TR, the flow was too fast at 120^{o}C. The melt flow indices of the resins depend on the molecular chain length. The longer the chain length means the higher amount of chain entanglement resulting in less mobility of the polymer chains and thus the higher the viscosity. The higher viscosity would lead to a lower melt flow index.[40]

The overall conversion of the solid copolymer was determined by gravimetric method. The conversions of these five copolymers were all above 90%.

The formulation of sample L16-TR with the monomer composition Sty/BA: 95/5 has been selected to continue for the next stage of study instead of L15-TR. This is because T_g of the final toner would become lower by a few degrees than that of the fixing resin after mixing with the other additives. So T_g of the fixing resin is preferably set at a few degrees higher than T_g of targeted toner.[9]

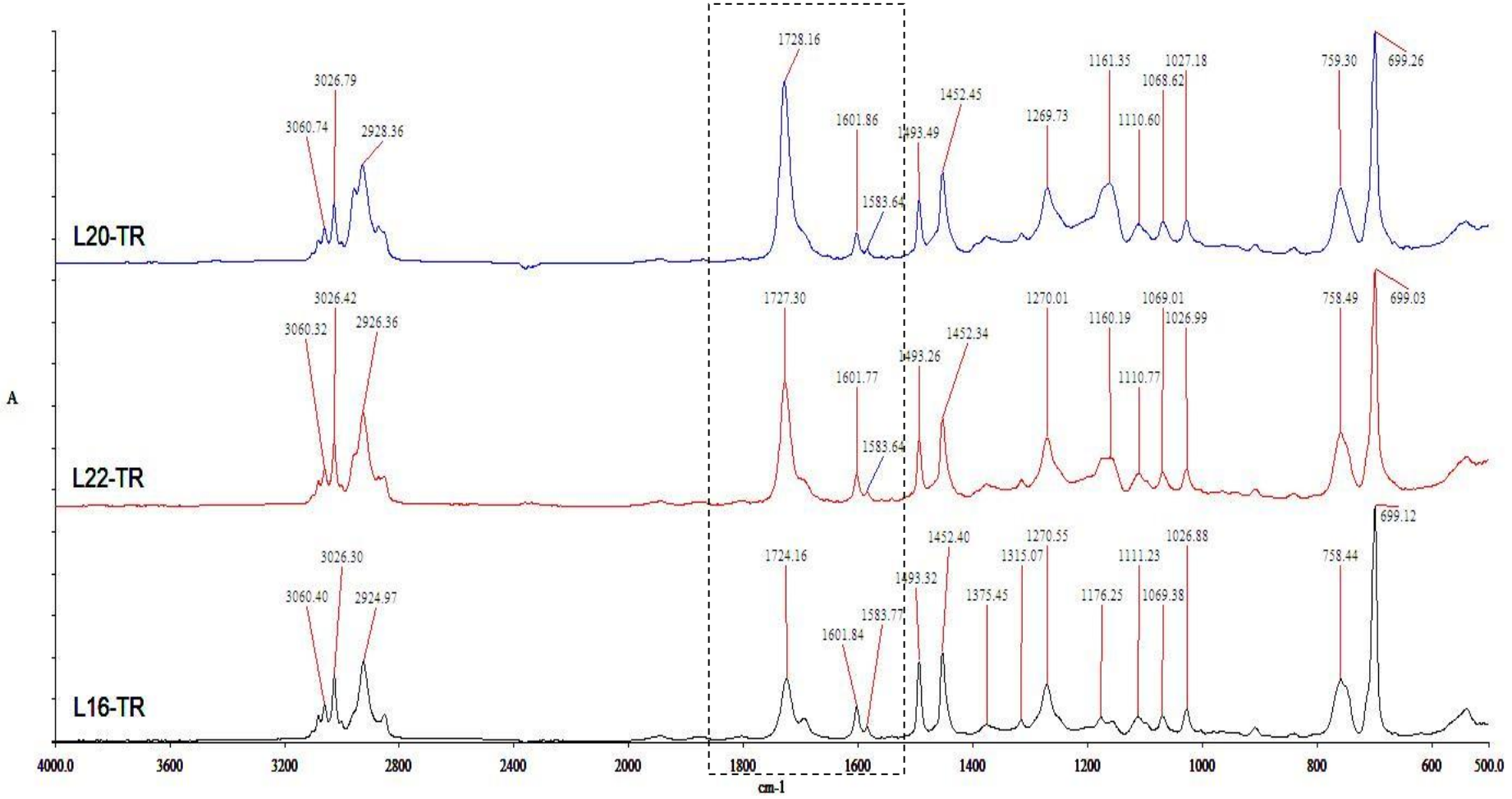


Figure 3.3: FT-IR spectra of L20-TR, L22-TR and L16-TR

Table 3.2: Effect of varying monomer ratios at constant initiator concentration

Sample Code	**L20-TR**	**L21-TR**	**L22-TR**	**L15-TR**	**L16-TR**
Formulations/ Parts per 100 parts of total monomers by weight					
Styrene	75	80	85	90	95
BA	25	20	15	10	5
Benzoyl Peroxide	15	15	15	15	15
Conversion/ %	93.71	94.36	92.53	94.58	91.15
Properties					
T_g/^oC	39	43	47	55	63
M_n/ x10^3Daltons	2.22	2.49	2.71	2.83	3.10
M_w/ x10^3 Daltons	4.07	4.75	5.36	5.74	6.43
M_p/ x10^3Daltons	1.16	1.97	2.70	2.89	3.80
M_z/ x10^3Daltons	7.53	8.57	9.69	10.55	11.54
M_w/M_n	1.84	1.91	1.98	2.03	2.07
MFI/ g/10min (120^oC)	Flow too fast	76.58	32.00	17.33	13.73

(1 Daltons = 1.66 x 10^{-27} kg)

3.1.2 Series 2: Different concentrations of initiator at constant monomer ratio

A free radical polymerization mechanism includes initiation, propagation, and chain transfer to monomer, and termination. Initiation involves formation of free radicals. Free radical initiators can be easily produced from thermal decomposition of added initiators. In this study, benzoyl peroxide was used as initiator.

In series 2, the effect of initiator concentrations of 5.0, 7.5, 10.0, 12.5, and 15.0 parts per 100 parts of total monomers was studied using the formulation as shown in Table 3.3. Copolymerization by using different concentrations of benzoyl peroxide was carried to investigate the change in molecular weight distribution by using different amounts of the

initiator. Excess of initiator would act as chain transfer agent. This is because low molecular weight polymer chains are produced with increasing initiator concentration.[22]

Low molecular resin should have a number average molecular weight (M_n) from 8.00×10^3 to 2.00×10^4 Daltons.[41] If the resin has a M_n of less than 8.00×10^3 Daltons, the anti-blocking properties of the toner may be lowered and fogging during the development process may occur. On the other hand, if the low molecular weight resin has a M_n above 2.00×10^4 Daltons, anti-blocking and anti-offset properties are lowered.

By increasing the benzoyl peroxide concentration, the M_n has shifted to lower value (Table 3.3). This is due to the increase in the amount of free radical generated and consequently the rate of polymerization increased proportionally as well as rate of chain termination by radical combination and chain disproportionation. Thus, the high initiation leads to the formation of shorter polymer chains, leading to a copolymer of lower molecular weight. In Table 3.3, the results show that this series of copolymers have M_n in the range of 3.10×10^3 to 1.00×10^4 Daltons.

As the molecular weight of the copolymer is lowered, the glass transition temperature of the resin decreases. Low molecular weight chains have more terminals per unit volume than longer chains, so the increased number of end groups will increase the chain mobility and free volume, lowering the T_g.[42] Thus, the T_g of the sample decreases when the amount of initiator is increased. It had proven by the DSC curves as shown in Figure 3.4 below. Extrapolation of T_g refer to Appendix C (Figure C.5-C.9).

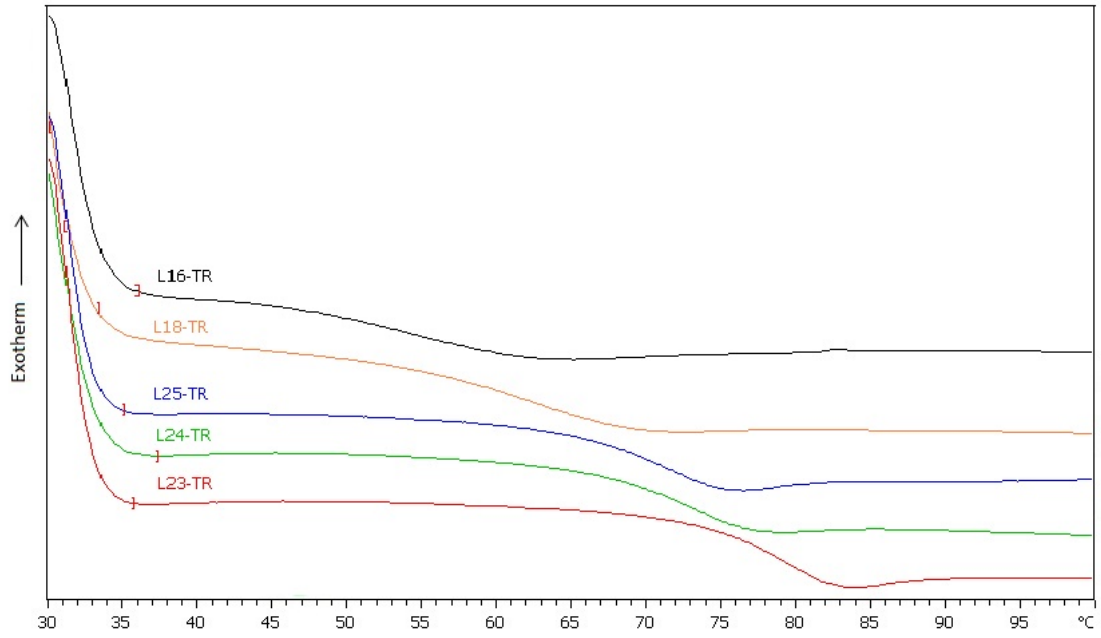


Figure 3.4: DSC thermogram of L23-TR, L24-TR, L25-TR, L18-TR and L16-TR at the heating rate of 10^{o}C/min

Copolymer L23-TR could not flow at 120^{o}C, indicating that this sample is more viscous than the others in this series. The viscosity of the sample increases as the molecular weight increases. The melt flow of the high molecular weight polymer is slower than the low molecular weight polymer at the same temperature.

As the amount of initiator was increased, the conversions of these five copolymers were around 93.0% at the same reaction time.

Both samples L16-TR and L18-TR have satisfied the requirements in terms of T_g and molecular weight distribution. Formulation of sample L18-TR has been selected to continue for the mixing process instead of L16-TR because higher initiator usage is uneconomically and large amount of residue of the polymerization initiator may contaminate the toner.[43]

Table 3.3: Effect of varying initiator concentration at constant monomer ratio

Sample Code	**L23-TR**	**L24-TR**	**L25-TR**	**L18-TR**	**L16-TR**
Formulations/ Parts per 100 parts of total monomers by weight					
Styrene	95	95	95	95	95
BA	5	5	5	5	5
Benzoyl Peroxide	5.0	7.5	10.0	12.5	15.0
Conversion/ %	93.58	94.92	93.71	92.98	93.15
Properties					
T_g/^oC	73	71	68	65	63
M_n/ x10^3Daltons	10.13	6.67	5.56	4.68	3.1
M_w/ x10^3 Daltons	23.06	15.58	12.97	10.28	6.43
M_p/ x10^3Daltons	22.61	14.31	10.93	8.66	3.80
M_z/ x10^3Daltons	35.51	25.28	21.24	17.05	11.54
M_w/M_n	2.28	2.34	2.30	2.20	2.07
MFI/ g/10min (120^oC)	Could not flow	2.87	4.64	12.00	13.73

(1 Daltons = 1.66 x 10^{-27} kg)

3.2 Synthesis of High Molecular Weight Styrene Acrylic Copolymer

3.2.1 Series 3: Different monomer ratio at constant AA, initiator and cross-linking agent concentration

Table 3.5 summaries the properties of the copolymers as a function of the different styrene: butyl acrylate ratios (Sty/BA = 70/28, 75/23, 80/18, 85/13, 90/8), while the amount of acrylic acid remains constant in this study. The total amount of monomers was 100 parts.

T_g of the copolymers increase as the amount of styrene increases from 45^{o}C to 69^{o}C (as shown in Figure 3.5). Extrapolation of T_g refer to Appendix C (Figure C.10-C.14). As the amount of bulky pendant group of styrene increases, it will hinder chain rotation and consequently higher temperature is required to supply sufficient energy for the transition to the rubber state.[44] Lower amount of styrene tends to cause a decrease of T_g which will lead

to unacceptably low toner resin blocking temperature and agglomeration of toner particles obtained from such resins.[45]

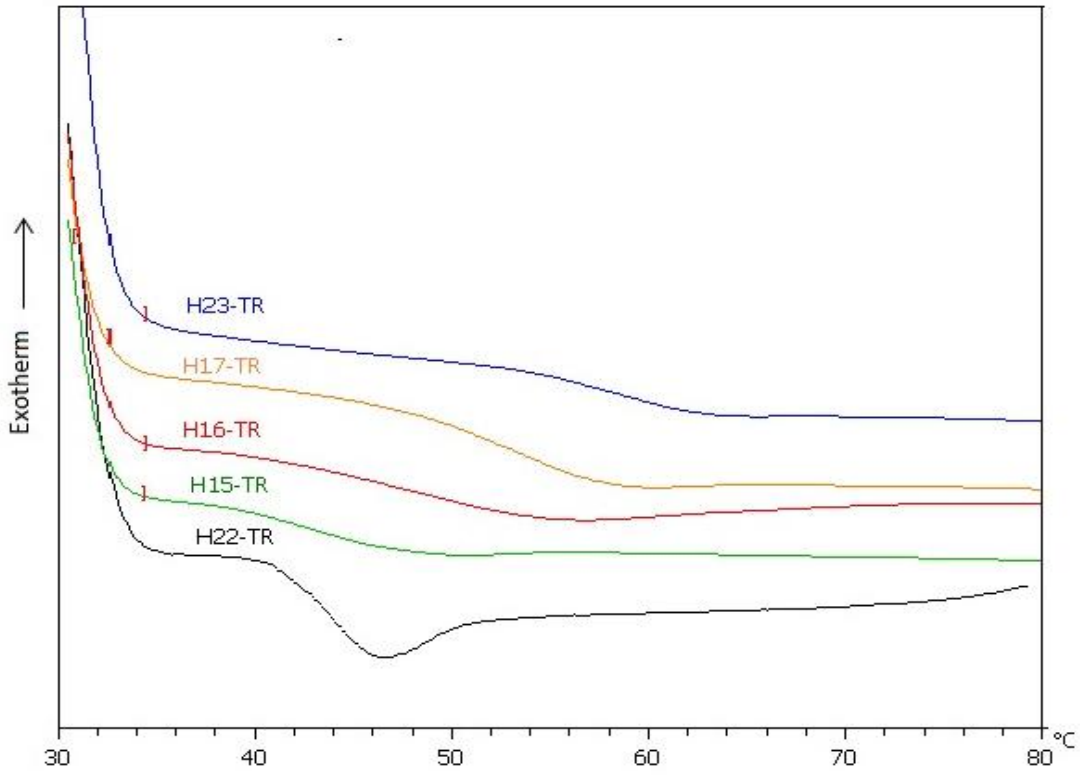


Figure 3.5: DSC thermogram of H22-TR, H15-TR, H16-TR. H17-TR and H23-TR at the heating rate of 10^{o}C/min

Figure 3.6 shows that the experimental and calculated T_g according to Fox equation and Gordon-Taylor equation, as a function of composition of the styrene. The contribution of acrylic acid in T_g was ignored, as the major chain structures were still from the styrene and butyl acrylate, while AA (in the smallest amount) just served to insert between the predominantly Sty-BA segments. The Fox equation does not fit the T_g of the copolymers well (with the deviation in T_g of approximately 2-18 K) compared with the Gordon-Taylor equation (with the deviation in T_g of approximately 1-11 K). Large T_g deviations from the Fox equation was due to this equation neglects the effects of interactions and chain

orientation on the composition dependence of T_g.[46] While for Gordon-Taylor equation, the value of k gives a qualitative measure of the degree of interaction between the components, the higher the value of k, the higher the degree of interaction.[47] Calculation of k refer to appendix I.

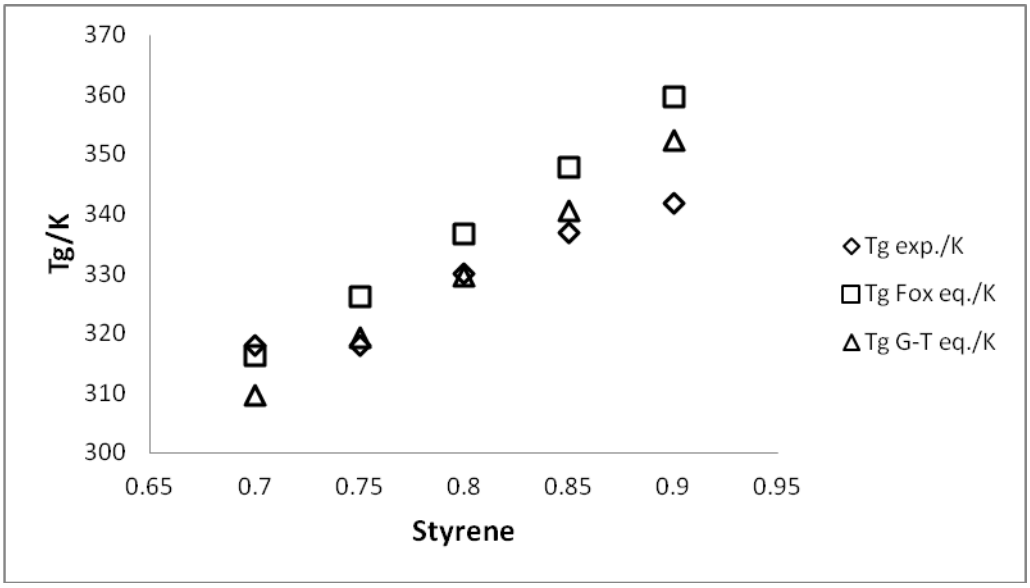


Figure 3.6: Comparison of T_gs of Styrene Acrylic Copolymers obtained from experimental and calculation by Fox equation and Gordon-Taylor equation (k=0.5461)

The FT-IR spectra of styrene-acrylate copolymer in different monomer composition with the addition of constant amount of acrylic acid are shown in Figure 3.7. Due to the low concentration of acrylic acid in the mixture, the presence of acrylic acid is hardly observed from the spectrum. The O-H stretching vibration at 3000-3500 cm^{-1} which is the characteristic peak of carboxylic acid is not seen in the spectrum.

The quantitative analysis of the FT-IR spectra was carried out by analyzing the absorption bands for the C-C group at 1601 and C=O groups at 1724 cm^{-1} to determine the monomer composition in the copolymer as discussed in section 3.1.1.

Table 3.4: FT-IR spectra peak area ratio of 1601 cm^{-1}/1724 cm^{-1} bands in the Styrene Acrylic Copolymers

Sample	**Ratio of Sty/BA/AA used**	**A_{1601}**	**A_{1724}**	**A_{1601} / A_{1724}**
H22-TR	78/28/2	0.05	0.33	0.15
H16-TR	80/18/2	0.05	0.20	0.25
H23-TR	90/8/2	0.04	0.07	0.57

From Table 3.4, **A_{1601} / A_{1724}** increases from 0.15 to 0.57 in agreement with the increasing content of styrene in the copolymer.

Regarding the molecular weight of the resin, M_w are within a range of 1.07 x 10^5 to 1.38 x 10^5 Daltons while M_n are within a range from 3.70 x 10^4 to 5.40 x 10^4 Daltons. Ratios of M_w/M_n, which indicate the polydispersity, are within 2.00 to 3.60. The molecular weight distribution measured by the GPC is represented by the soluble fraction in THF. The gel fraction (insoluble in THF) could not be measured by the GPC.

In contrast to the earlier series, this set of copolymers was prepared with relatively low initiator concentration. Thus as expected, the molecular weight has increased significantly resulting in fraction that was insoluble in THF. The percentage of THF insoluble fraction or gel content was in the range of 9.20 to 18.70%. These high molecular weight fraction is good to impart hot offset resistance and low temperature fixability to the toner.[48]

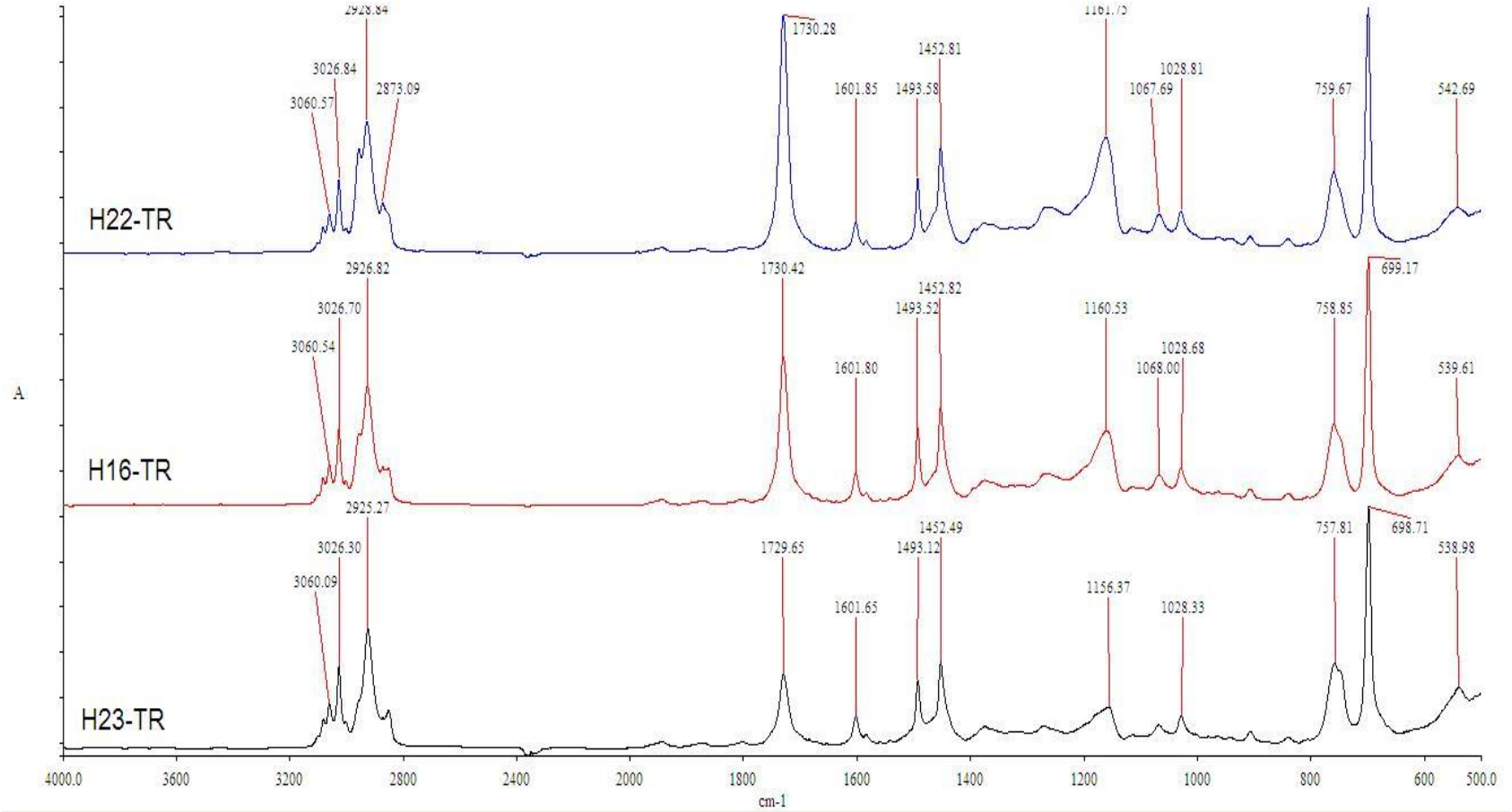


Figure 3.7: FT-IR spectra of H22-TR, H16-TR and H23-TR

Table 3.5: Effect of varying monomer ratio at constant AA, initiator and cross-linking agent concentration

Sample Code	**H22-TR**	**H15-TR**	**H16-TR**	**H17-TR**	**H23-TR**
Formulations/ Parts per 100 parts of total monomers by weight					
Styrene	70	75	80	85	90
BA	28	23	18	13	8
Acrylic Acid	2	2	2	2	2
Benzoyl Peroxide	1	1	1	1	1
Cross-linking Agent	0.1	0.1	0.1	0.1	0.1
Conversion/ %	94.14	94.58	94.40	92.25	93.89
Properties					
T_g/^oC	45	46	57	64	69
M_n/ x10^4 Daltons	3.70	3.67	3.66	4.09	5.40
M_w/ x10^4 Daltons	11.40	11.71	12.24	13.76	10.71
M_p/ x10^4 Daltons	7.24	63.38	7.84	7.26	7.37
M_z/ x10^4 Daltons	28.46	29.33	36.96	50.53	20.45
M_w/M_n	3.08	3.19	3.61	3.37	1.98
MFI/ g/10min	16.14	9.92	7.06	4.35	2.58
Acid Number /mg $KOHg^{-1}$	4.75	4.70	4.36	3.54	3.32
% THF Insoluble Fraction/ %	10.12	12.39	18.71	13.46	9.26

(1 Daltons = 1.66 x 10^{-27} kg)

As the amount of BA increased, the melt flow index has increased. Melt flow indexes are in the range of 2.6 to 16.1 g /10 min. Flow occurs when the polymer molecules can slide past each other. The ease of flow depends upon the mobility of the molecular chains and the forces of entanglements holding the molecules together. Flow properties mainly depend on the molecular structure.[49] The aromatic ring from styrene hinder the polymer chain rotation, therefore H23-TR have the lowest value of MFI.

Toner resins need to have certain acid number in order to improve the fixing performance. In this project, 2.0 parts of acrylic acid was added into the high molecular weight system. The acid numbers in this series are fairly close to each other, from 3.30 to 4.80 mg KOH/g, as it was the contribution from acrylic acid. This is the level recommended by patent literature, if the resins with acid values less than 0.1 mg KOH/g will encounter difficulty in production and toner made of resin with an acid value exceeding 20 mg KOH/g tends to have lower humidity resistance. [50]

3.2.2 Series 4: Different Concentration of Cross-linking Agent at constant monomer ratio and initiator concentration

A plausible scheme for the synthesis of cross-linked styrene-acrylate copolymer is represented by Figure 3.8. Modification of styrene-acrylate copolymer structure by addition of cross-linking agent is to improve offset resistance of toner. The cross-linked copolymer comprises cross-linked portions and linear portions. The highly cross-linked gel particles are uniformly distributed in the linear portions.[47]

The effect of the cross-linking agent (CLA) was investigated using the formulations shown in Table 3.6. Five runs were carried out using different amounts of cross-linking agent (0.1, 0.2, 0.3, 0.4 and 0.5 parts per 100 parts of total monomers).

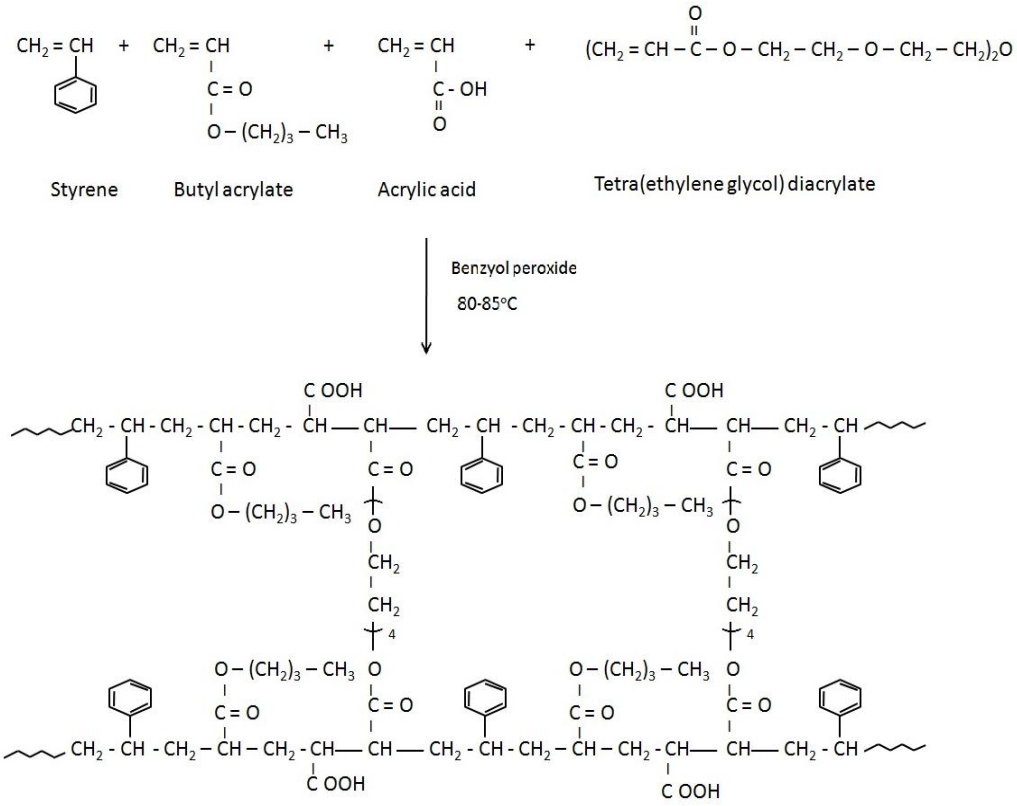


Figure 3.8: Plausible cross-linking reaction to form cross-linked Styrene Acrylic Copolymer

Higher amount of cross-linking agent has shifted the molecular weight distribution towards lower values, because of the formation of gel or insoluble polymer fraction.[51] Larger fraction of the long chains is tied up in the network, which presumably was insoluble in THF, so the actual molecular weight distribution could not be measured by GPC. Only the portion comprise of low molecular weight resin that was soluble in THF could be measure by GPC.

The percentage of highly cross-linked gel particles was determined by its insolubility in THF. The gel fraction is in the range of 13.0 to 17.0%. But there is a rapid increase for sample H19-TR, where the gel fraction is 68.0%. Large amount of the copolymer has become insoluble, but only swell in THF when the amount of cross-linking agent is increased to 0.3 parts.

When cross-links are introduced into a polymer, the molecular mobility was restricted and T_g rises. For a lightly cross-linked case, the T_g is found to increase linearly with number of cross-links.[44] Experimentally, the T_g values are in the range of 64-65^oC which are relatively constant (as shown in Figure 3.9), irrespective of the concentrations of the cross-linking agent, when the monomers ratios were maintained the same. Extrapolation of T_g refer to Appendix C Figure C.13, C.15 and C.16).

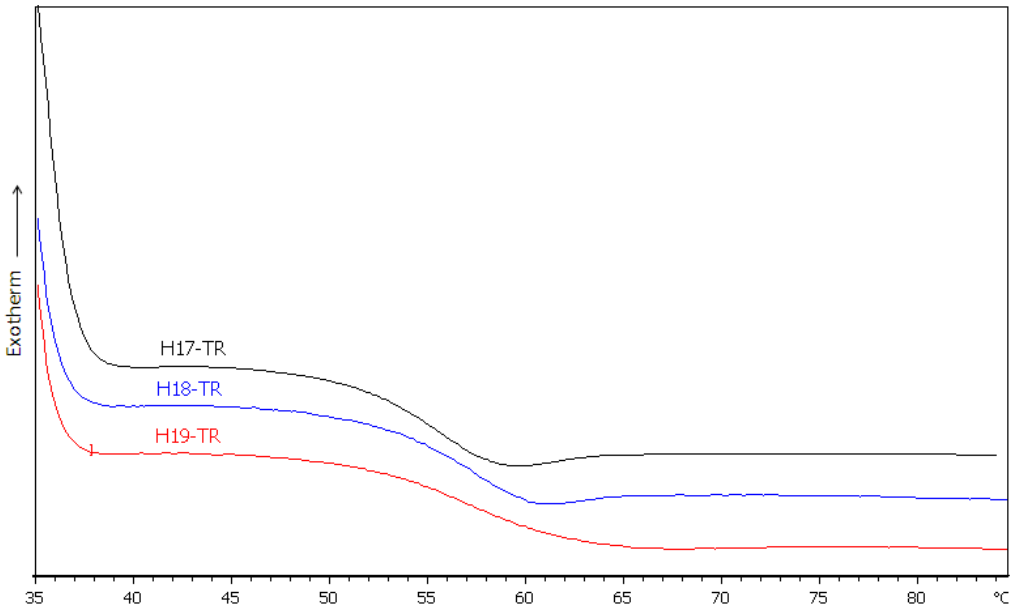


Figure 3.9: DSC thermogram of H17-TR, H18-TR and H19-TR at the heating rate of 10^oC/min

Samples H20-TR and H21-TR aggregated to form lump after 360 minutes and 240 minutes of reaction time respectively after addition of CLA. Kiatkamjornwong et al. explained that the clustered lump forms indicate the high molecular weight as a result of the gel effect at low conversion during styrene-divinylbenzene copolymerization.[52] This is due to the very high viscosity of the medium causing extensive entanglements by the cross-linking which hinder the movement of the active chain end into position where it could react with another radical end. [34]

Cross-linking involves a significant increase in viscosity. The viscosity of a polymer depends on the molecular chain length. The longer the chain the more chance there is of chains becoming tangled and hence the higher the viscosity and so the lower the melt flow index.[40] In this study, sample H17-TR has a MFI of 4.35 g/10 min at 150^{o}C, but samples H18-TR and H19-TR could not flow at this temperature due to high viscosity. These two samples could not flow at 150^{o}C, unless the measured temperature is increased. Sample H18-TR and H19-TR has a MFI of 4.41 g/10min at 160^{o}C and 5.34 g/10 min at 170^{o}C.

The acid values of the samples are fairly close to each other; presumably the amount of acrylic acid used in this formulation was kept constant. The acid values of this series only represent the soluble fraction of sample in THF. It is preferable to have an acid value exceeding 3.0 mg KOH/g. By increasing the acid value to exceed a certain level, it becomes possible to form sufficient cross-linking structure, thereby preventing the deterioration of the anti-offset characteristic and alleviating the difficulties caused by a lowered dispersibility of the other components in the toner.[53]

The percentage of conversion for this study is above 92.0%. In commercial production, higher conversion must be achieved to ensure lower lost due to un-reacted monomers. Percentage of conversion of more than 90.0% is considered satisfactory because suspension polymerization usually produces a product with relatively high residual monomer content.[54]

Both samples H18-TR and H19-TR have satisfied the requirements in terms of T_g. But formulation of sample H18-TR has been selected to continue for the mixing process instead of H19-TR is because of the gel fraction of H19-TR being too high.

Table 3.6: Effect of varying cross-linking agent concentration at constant monomer ratio and initiator concentration

Sample Code	**H17-TR**	**H18-TR**	**H19-TR**	**H20-TR**	**H21-TR**
Formulations/ Parts per 100 parts of total monomers by weight					
Styrene	85	85	85	85	85
BA	13	13	13	13	13
Acrylic Acid	2	2	2	2	2
Benzoyl Peroxide	1	1	1	1	1
Cross-linking agent	0.1	0.2	0.3	0.4	0.5
Conversion/ %	92.25	94.33	93.95	-	-
Properties					
T_g/^oC	64	64	65	-	-
M_n/ x10^4 Daltons	4.09	3.47	3.45	-	-
M_w/ x10^4 Daltons	13.76	21.85	18.99	-	-
M_p/ x10^4 Daltons	7.26	8.59	5.25	-	-
M_z/ x10^4 Dalton	50.53	80.23	87.52	-	-
M_w/M_n	3.37	6.30	5.50	-	-
MFI/ g/10min (150^oC)	4.35	Could not flow	Could not flow	-	-
Acid Number /mg $KOHg^{-1}$	3.54	4.03	2.34	-	-
% THF Insoluble Fraction/ %	13.46	16.85	67.93	-	-
Coalescence time/min	-	-	-	360	240

(1 Daltons = 1.66 x 10^{-27} kg)

Coalescence time = the period of time when the copolymer beads started aggregate to form lump after the reaction start

3.3 Mixing High Molecular Weight and Low Molecular Weight Styrene Acrylic Copolymers.

The mixing of high molecular weight and low molecular weight fractions at different ratios (HMW/LMW = 50/50, 60/40, 70/30, 80/20, 90/10) was studied using the formulation shown in Table 3.7. The high molecular weight toner resin and low molecular weight toner resin used in this study are H18-TR and L18-TR respectively.

Binder resins used in the production of offset-free toners are required to be as tough as possible. To meet this requirement, high molecular weight resins are usually employed. However, their presence in toner formulation is detrimental to the initial fixing of the toner. To counter this, blending different molecular weight resins is a common method of modifying the fusing properties of a toner. A broad molecular weight distribution or a blend of low molecular weight and high molecular weight resins has been shown to allow high offset temperatures while retaining low minimum fixing temperatures.[55]

In Figure 3.10, overlaid GPC chromatograms are shown consisting of high molecular weight resin, low molecular weight resin and blended resin which are H18-TR, L18-TR and M10-TR respectively. The blended resin can have a peak in both the low molecular weight region and the high molecular weight region, or termed as “bimodal distribution”.

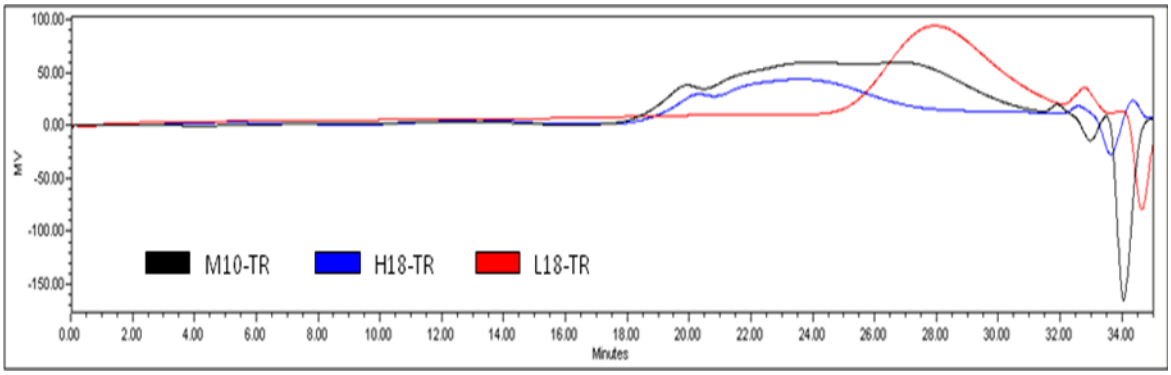


Figure 3.10: GPC profiles of H18-TR, L18-TR and M10-TR

Depending upon the blending ratio and the peak molecular weight of the high molecular weight to be blended, even though the gel fraction of the mixture is above 8.0%, the bimodal distribution of the soluble fraction is obvious for sample M08-TR to M11-TR with some overlap between high molecular weight and low molecular weight portions (refer Figure 3.11). By increasing the weight fraction of low molecular weight copolymer, the shape of the molecular weight distribution curve becomes broader. The molecular weight distribution of sample M12-TR shows one broad peak as the content of low molecular weight was too low.

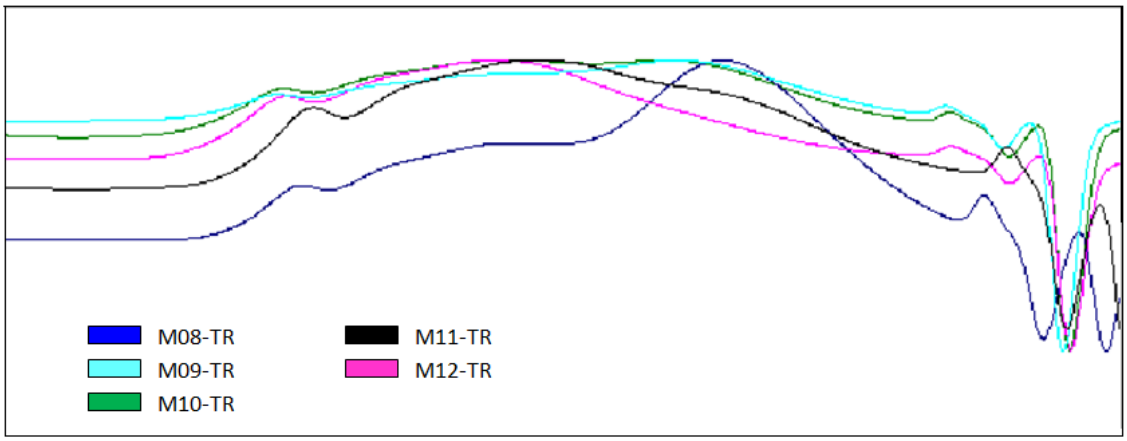


Figure 3.11: Comparison of GPC chromatogram of Blended Resins at different blending ratios

T_g of the mixture will depend upon the ratio of two components. Higher content of low molecular weight portion increases free volume because the number of polymer chain ends increases. Thus, as the low molecular weight portion increases, T_g of the mixture also decreases. The mixture was assumed to be miscible as they have made from the same monomers and the DSC thermogram shows only one T_g (refer Figure 3.12). Extrapolation of T_g refer to Appendix C (Figure C.17-C.21).

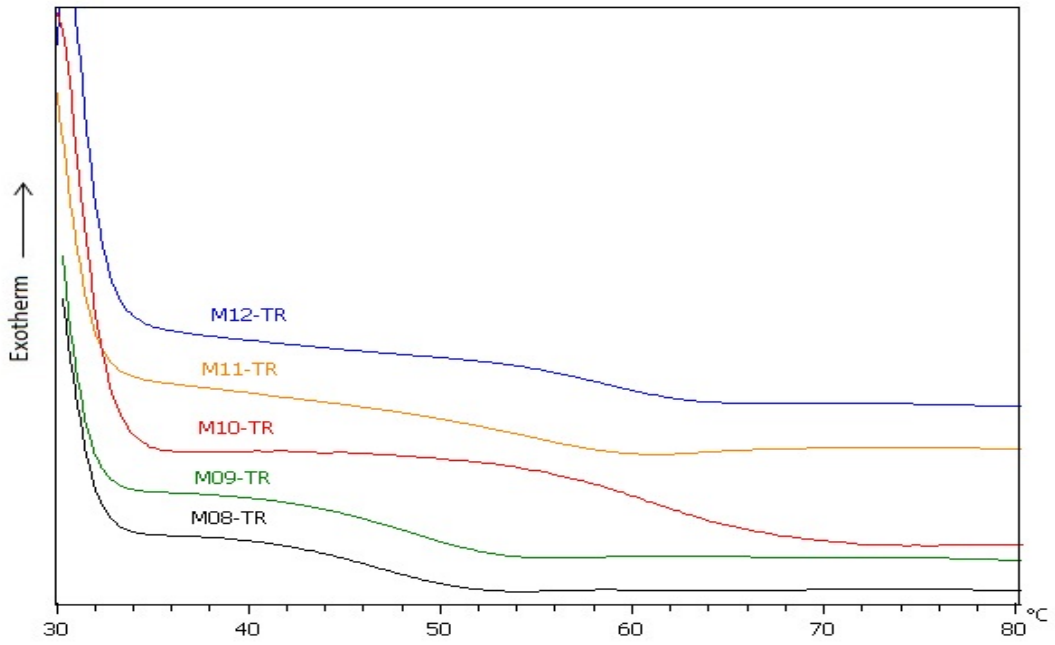


Figure 3.12: DSC thermogram of M08-TR, M09-TR, M10-TR, M11-TR and M12-TR at the heating rate of 10^{o}C/min

Melt flow indexes of the blended resin had become lower as the ratio of the high molecular weight portion is higher, due to higher amount of gel fraction in the mixture. Melt flow index was in the range of 13.0 to 55.0 g/10 min at 150^{o}C. In addition, melt flow index value of toner resin was important in toner processing especially to determine the conditions of kneading process.

The resin must have a certain acid number in order to increase charging ability of toner. As the high molecular weight portion increases, acid number of the mixture also increases from 2.5 to 3.4 mg KOH/g. It can be attributed to the acrylic acid added in the preparation of high molecular weight resin.

Samples M09-TR, M10-TR and M11-TR have been selected to continue for the pilot plant process to produce toner as they satisfy the requirements in terms of T_g, molecular weight distribution, and melt flow index value.

Table 3.7: Effect of blending High Molecular Weight and Low Molecular Weight Copolymers at different ratios

Sample Code		**M08-TR**		**M09-TR**		**M10-TR**		**M11-TR**		**M12-TR**
Mixing Ratio	**High**	50		60		70		80		90
	Low	50		40		30		20		10
T_g/ ^oC		55		56		61		64		69
Molecular Weight		**High**	**Low**	**High**	**Low**	**High**	**Low**	**High**	**Low**	
M_n/ x10^3 Daltons		83.74	4.85	101.28	6.96	101.37	7.35	56.97	4.05	33.81
M_w/ x10^3 Daltons		204.79	10.55	281.77	14.89	316.16	15.01	182.59	7.14	233.12
M_p/ x10^3 Daltons		30.61	9.12	37.70	15.85	61.49	18.81	59.22	15.70	77.36
M_z/ x10^3 Daltons		579.28	16.32	939.36	21.68	1107.99	21.16	659.13	9.74	992.9
M_w/M_n		2.45	2.18	2.78	2.14	3.12	2.04	3.21	1.76	6.90
GPC Peak ratio		41.56	58.44	50.65	49.35	59.48	40.52	75.04	24.96	-
MFI/ g/10min (150^{o}C)		54.92		45.81		29.64		15.48		12.76
Acid Number /mg $KOHg^{-1}$		2.51		2.70		3.02		3.16		3.40
%THF Insoluble Fraction		8.96		9.38		9.38		12.78		13.39

3.4 Properties Results of toner

Table 3.8 shows the properties of three toners. Blended resins from section 3.3 which are M09-TR, M10-TR and M11-TR were used as material to produce toner for this study. The same formulation (refer to section 2.4.3) had been used to produce these three toners.

Particle diameter of commercial toners, D_{50} is usually in the range from 8.0-13.0 µm. D_x (x = 5, 50 or 95) was based on volume and the particle diameters at which a cumulative percentage of 50% of the total particles are attained are defined as volume D_{50}, and the particle diameters at which a cumulative percentage of 5% and 95% are attained are defined as volume D_5 and volume D_{95} respectively.[56] Ratio of D_{95}/D_5 indicates the degree of sharpness of a particle size distribution. The particle diameter of toner, D_{50} was controlled at 9.0±0.5 µm during milling and classification process. Therefore, the particle diameters, D_{50} of these three toners are in the range of 8.50-9.80 µm. Particle size distribution data sheet of toners refer to Appendix F (Figure F.1-F.3).

A toner composition also includes a portion of fine particles which referring to toner particles having a particles size of less than 5 µm and a portion of coarse particles which toner particle size more than 24 µm. The number percentage of particles of 5 µm and number percentage of particles of 24 µm based on a total number of particles was maintained low to avoid affect the image quality. Particle size distribution (PSD) determines the image resolution and background density. Large toners make sharp edges in images look blurry.[57] Small toners have low fluidity due to cohesion, increase in charge-to-mass ratio (q/m) and low cleaning efficiency.[58]

Tribocharge of toner is a major factor in electrophotographic process, and charge control agent (CCA) is used for toners to improve their tribocharging characteristics. Typical tribocharge values are 10-40 μC g^{-1}.[2] The tribocharge value of these three toner is in the range of 17.0 to 23.0 μC g^{-1}. Negative value of tribocharge value indicates those toners are charged negatively. M11-FT have higher acid value as it contains higher portion of high molecular weight resin and acid value help to increase charging ability of toner.

The charging behavior of the toner with CCA is affected by many factors, such as particle size, affinity of CCA with resin, process condition and environmental condition.[58] For this study, the concentration of CCA remains constant, so the value of tribocharging is fairly close to each other. Lee et al. reported that the charging level of toner did not increase continuously as the content of CCA increases.[59] Each CCA has optimum charging level and those values are dependent with CCA type.

Magnetic content, apparent density and wax content of these three toners were closes to each other; presumably the same amount of magnetic pigment and wax had been used in toner formulation.

M09-FT, M10-FT and M11-FT have the same flowability, able to flow through a 5 mm disc. Toner flow describes how toner behaves in contact with itself (cohesion). Thus, flowability test is a good guide for identifying toners with improved transfer.

Table 3.8: Properties Results for toners

Sample Code	**M09-FT**		**M10-FT**		**M11-FT**	
Toner Resins used	M09-TR		M10-TR		M11-TR	
Particle Size Distribution						
5% / µm	4.38		5.50		5.02	
50% / µm	8.52		9.79		9.49	
95% / µm	15.70		18.06		17.39	
5 µm / %	8.39		2.97		4.91	
24 µm / %	99.90		99.62		99.75	
Sharpness Index, D95/D5	3.58		3.28		3.46	
Molecular Weight	**High**	**Low**	**High**	**Low**	**High**	**Low**
M_n/ x10^3 Daltons	80.08	4.57	66.07	4.46	57.72	4.35
M_w/ x10^3 Daltons	250.22	9.84	171.49	8.55	157.14	7.78
M_p/ x10^3 Daltons	27.25	9.57	65.87	11.81	65.33	16.96
M_z/ x10^3 Daltons	1072.53	14.99	492.71	12.12	514.37	10.57
M_w/M_n	3.12	2.51	2.59	1.92	2.72	1.79
GPC Peak ratio	46.33	53.67	67.37	32.63	72.97	27.03
Tribocharge / µC g^{-1}	-22.0		-19.5		-17.0	
Magnetic Content /%	43		40		45	
Flowability / mm	5		5		5	
Apparent Density / g cm^{-3}	0.497		0.486		0.545	
T_g/ ^oC	53		59		75	
Wax Melting Point, T_p/^oC	154.81		136.81		147.18	
Wax Content/ %	0.93		0.94		0.98	
MFI/ g/10 min (160^oC)	25.56		12.60		7.98	

(1 Daltons = 1.66 x 10^{-27} kg)

Sample M11-FT has the highest T_g, which is 75^oC as expected. As the T_g is dependent on molecular weight, therefore, M11-FT with higher ratio of high molecular weight copolymer has high T_g. However, the T_g is excess of 70^oC and the fixability of M11-FT can be adversely affected. T_g of M10-FT fulfils the requirement properties of toner, which was in the range of 50-65^oC.[14]

Melt flow indexes of these three toners were in decreasing trend from samples M09-FT to M11-FT. M11-FT contained higher percentage of high molecular weight fraction and hence the higher the viscosity and so the lower the melt flow index.[40] This result shows that the ability of flow for M09-FT is better than the rest.

Figures 3.13, 3.14 and 3.15 show the pictures of the toner particles taken by Leica microscope under magnification 40X and 100X accordingly. The toner particles are found in irregular shape as expectedly, because it was pulverized mechanically.[1]

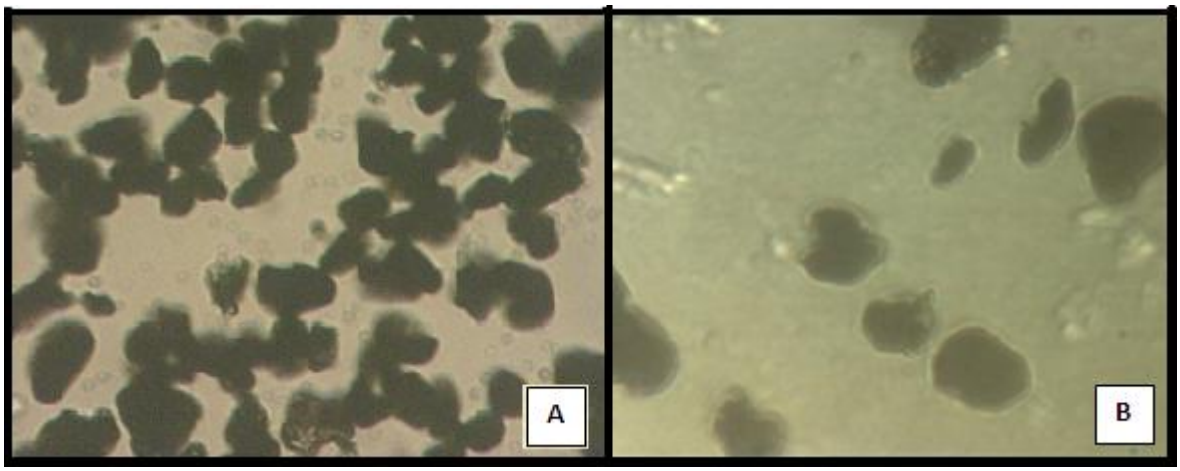


Figure 3.13: M09-FT (A: under magnification 40X, B: under magnification 100X)

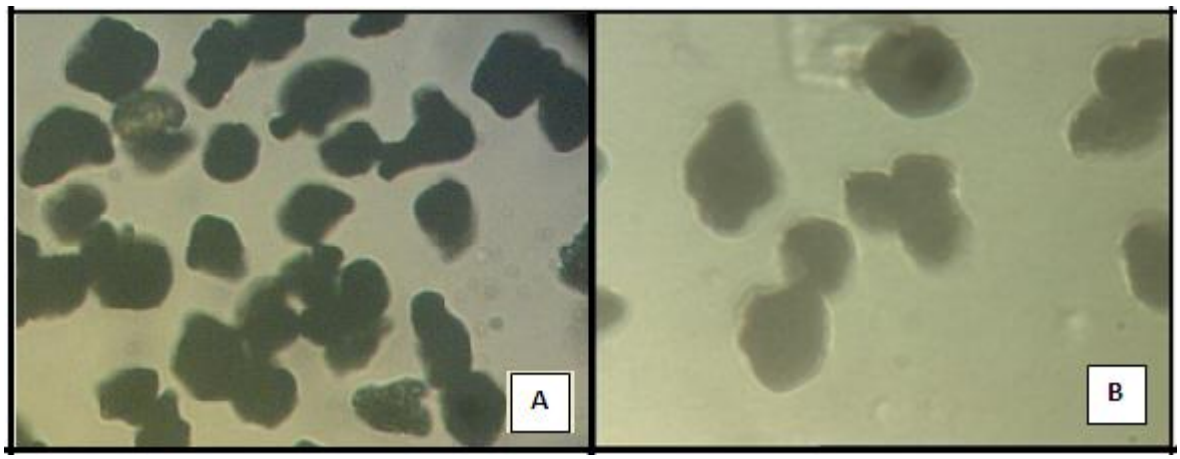


Figure 3.14: M10-FT (A: under magnification 40X, B: under magnification 100X)

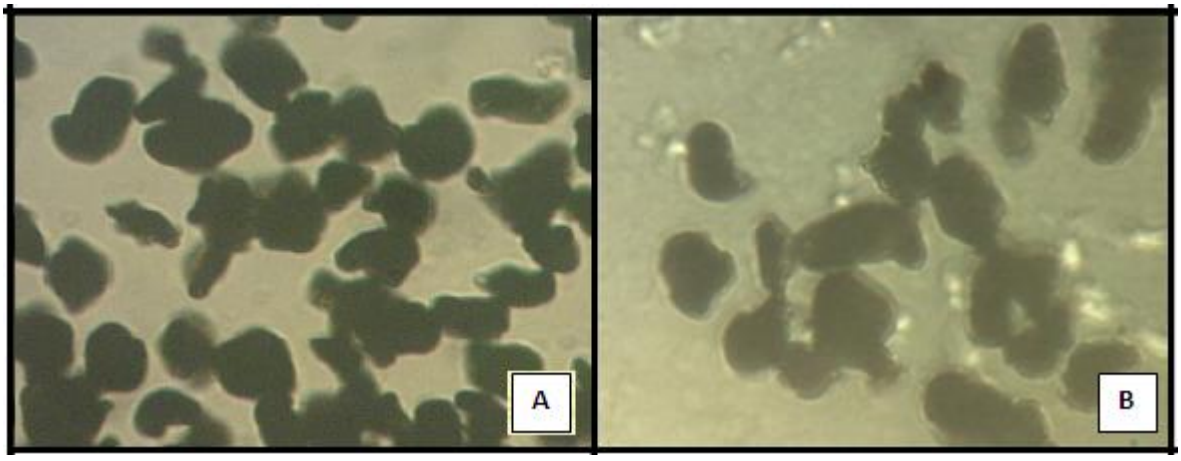


Figure 3.15: M11-FT (A: under magnification 40X, B: under magnification 100X)

Figure 3.16 shows the thermogravimetric analysis (TGA) curves for the three toners measured at the heating rate of 30 ^{o}C/min. The TGA curves showed two degradation steps. The first step weight loss is due to the degradation of toner resin in the temperature range of 300 – 450^{o}C and the second step weight loss can be attributed to degradation of wax and other additives. It confirms that the first and second step is correlated with the amount of toner resin and additives in the toner formulation. The higher residue amount was attributed to magnetite pigment which was around 44.0% in the toner formulation.

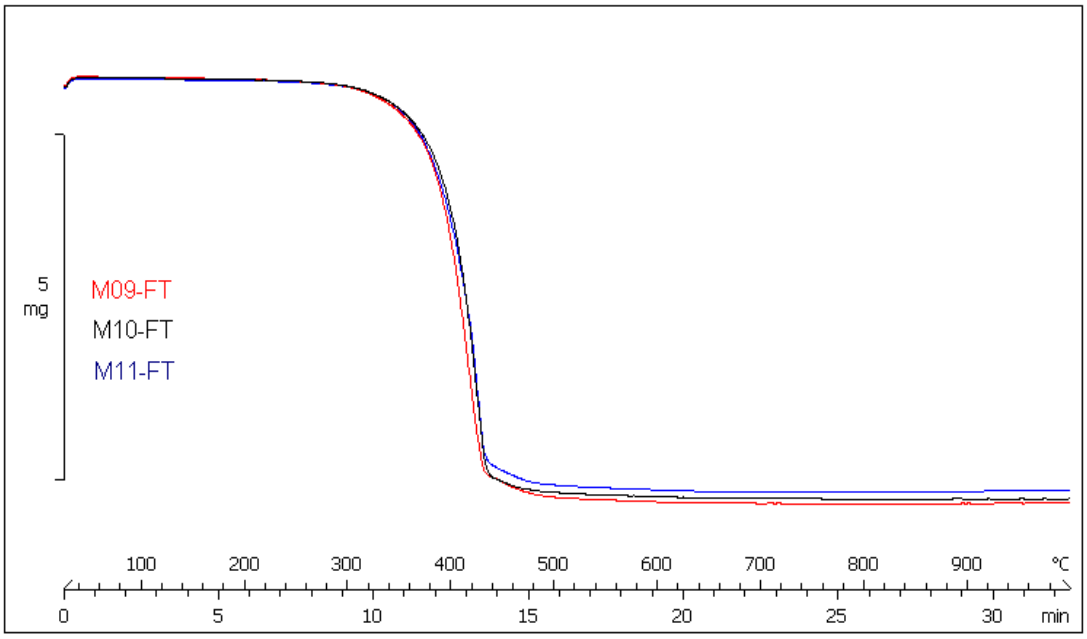


Figure 3.16: TGA curves of M09-FT, M10-FT and M11-FT at the heating rate of 30^{o}C/min

The percentage of weight loss drops as the amount of high molecular weight copolymer portion increase (refer to Table 3.9). Since the fraction of low molecular weight copolymer which undergoes easier degradation is decreased, the rate of weight loss must also decrease. A small weight loss, 1.6 – 3.1% occur around 450 - 500^{o}C in all cases which may due to the degradation of wax and other additives. The wax used in the toner formulation was low molecular weight polypropylene, and it undergone degradation at temperature around 500^{o}C.[60] While for charge control agent, is a type of chromium azo complex which the organic part of CCA decompose at 350^{o}C and only metal oxide remain as residue.

Table 3.9: Percentage weight loss of toners at different temperature region obtained from TGA at the heating rate of 30°C/min

Temperature region/ °C	**weight loss in this region/ %**		
	M09-FT	**M10-FT**	**M11-FT**
300 – 450	56.54	53.77	52.58
450 – 500	3.13	1.59	2.30
Residue	38.53	43.12	43.26

The thermal decomposition temperatures of toners, T_d were calculated from the first derivative of TGA curves and these values have been given in the Table 3.10. Thermal decomposition temperatures of toners were increased from 422°C to 432°C when the amount of high molecular weight copolymer portion was increased, presumably due to the contribution of some cross-linking and higher content of aromatic rings.[61] Second decomposition temperature of toner was due to degradation of CCA. The TGA curves of CCA (refer Appendix D, Figure D.5) shows second degradation step occur around 400 - 600°C. Sample M11-FT had higher second decomposition temperature was due to impurities of the sample.

Table 3.10: Thermal decomposition temperature of toners obtained from TGA at the heating rate of 30°C/min

Sample	**T_{d1}/ °C**	**T_{d2} /°C**
M09-FT	422.39	465.63
M10-FT	429.71	467.43
M11-FT	432.25	503.23

The test print results of three toners were attached in Appendices H, I and J accordingly. Print quality is mainly determined by the quality of combination of toner, paper, and printer, as well as the quality of the text and images that result. Therefore, the

print quality of the three toners may be affected by toner characteristics and cartridge used. Print quality will be evaluated by visual observation.

First page of print test image shows the summary of test target which include A to Z characters, different symbols, solid area and gray area, and different percentages of halftones, designed to evaluate print quality (as shown in Figure 3.17[A]). Test print for M09-FT and M10-FT show not much print defects, but severe banding occurs across the page vertically from first page to last page for M11-FT.

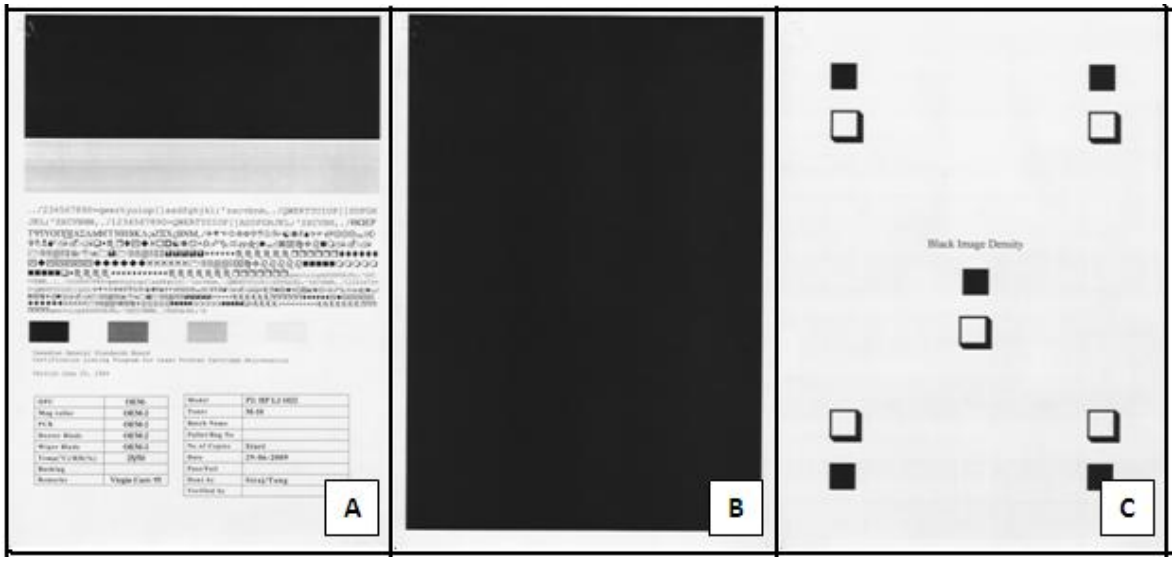


Figure 3.17: Example of test images template (A: text target, B: black page uniformity, C: image and background density target)

Figure 3.17[B] shows the test image designed to evaluate black (100% halftone) page uniformity. M10-FT shows the great uniformity in darkness, while the print of M09-FT appears uneven in inking. M11-FT produce severe banding image and grey toner spots on the whole paper. The different uniformity in darkness was due to uneven charge distribution of the toner and lead to poor developing problem, which the friction charge rate

of the toner cannot follow the consumption rate of the toner when printing is performed consuming a large amount of toner in a short time or continuous solid pattern printing.[62]

Image density (ID) evaluations were made in the one inch square blocks at different locations within at page (as shown in Figure 3.17[C]). The results from the Table 3.11 show that the ID values of M09-FT and M10-FT are close to each other and higher than M11-FT. The difference in the density comes from the q/m values of the toner charge. Therefore, M09-FT and M10-FT with more highly charged could transfer more toner to the paper.[12] Target ID value is 1.50; therefore, M09-FT and M10-FT have fulfill the requirement.

Table 3.11: Image density values of the three print test images

Sample Code	**Image Density (ID)**					**Average**
	Left Top	**Left Bottom**	**Center**	**Right Top**	**Right Bottom**	
M09-FT	1.61	1.53	1.63	1.55	1.60	1.58
M10-FT	1.58	1.55	1.62	1.53	1.57	1.57
M11-FT	1.49	1.43	1.42	1.06	1.27	1.33

Background density (BD) measurements were made on the open areas of the one inch square hollow blocks. M11-FT has the lowest BD value which indicates it gives little background hollow fog only (as shown in Table 3.12). The standard value of BD is up to 0.11. The three synthesized toners give higher values of BD than the standard value. This may due to poor distribution of CCA. The amount of CCA on the toner surface was

affected by the melt mixing condition and their affinity with the toner resin.[63] When the toner dispersion is not homogeneous, unbalanced charges will give poor image quality. Overcharge toner will prints light; undercharged toner prints dark and cause print background.

Table 3.12: Background density values of the three print test images

Sample Code	**Background Density (ID)**					**Average**
	Left Top	**Left Bottom**	**Center**	**Right Top**	**Right Bottom**	
M09-FT	0.13	0.13	0.13	0.13	0.14	0.13
M10-FT	0.13	0.13	0.14	0.13	0.14	0.13
M11-FT	0.12	0.13	0.11	0.12	0.13	0.12

Different percentages of halftone (5%, 10%, 20%, 25%, 30%, 40%, 50%, 60%, 70%, 75%, 80%, 90%, and 100%) is to check how accurately the printing system renders the tonal range from highlights to shadows (as shown in Figure 3.18[A]). The three test prints show good tone reproduction. The test prints of M11-FT show banding defects. At the same page, line quality was measured with horizontal and vertical lines at different width. It is found that the edge sharpness and raggedness produced by M09-FT and M10-FT are better than those from M11-FT because the formers have a higher image density.

Figure 3.18[B] shows the text image designed to evaluate tone reproduction, line edge raggedness and sharpness and resolution. Resolution depends on the particle size distribution.[57] Thus, three test prints have the same resolution as their particle size

distribution is close to each other. Print quality of M11-FT has been affected by banding and the image becomes blurring. Repetitive marks are found in left side of print images of M10-FT and M11-FT.

The fully black page shows severe defects; a more subtle blemish is observed on the gray page (25% halftone), as the eye is more sensitive to light gray color.[19] The test image template was shown in Figure 3.18[C]. The test prints of M09-FT and M10-FT show banding vertically and horizontally with repetitive marks. While print of M11-FT shows severe banding vertically with grey toner spots on the page.

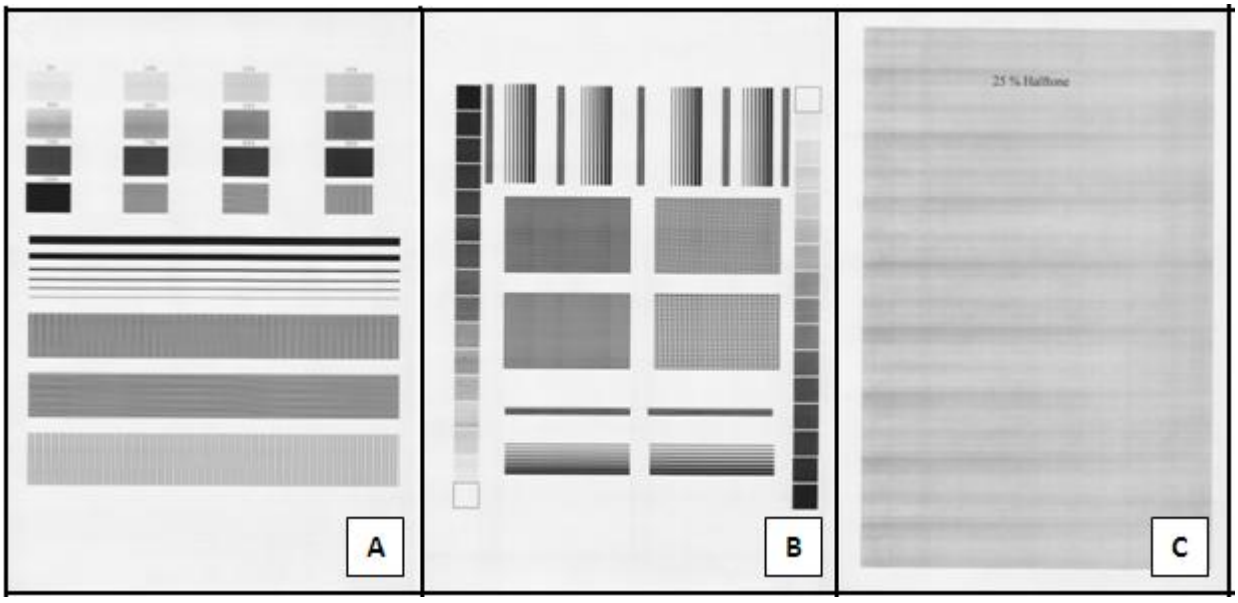


Figure 3.18: Example of test images template (A & B: tone reproduction, line edge raggedness and resolution test target, C: gray page uniformity)

Figure 3.19[A] is designed to check the severity of thermal banding.[64] When a solid area is printed and followed by a halftoned region, the area followed by a black stripe is significantly darker than after a white stripe. This thermal banding effect occurs in prints of M09-FT and M10-FT. Many thin grey lines appear in halftoned region of print M11-FT.

5% area coverage image full of alphabets ‘E’ (as shown in figure 3.19[B]) was used to evaluate toner yield. The reason for this is that ‘E’ is the most frequently used character in the English language. The target shown in Figure 3.19[C] is from ISO 19752 and is used for the same purpose too. The test print of M10-FT shows positive ‘E’ ghost image in the gray background.

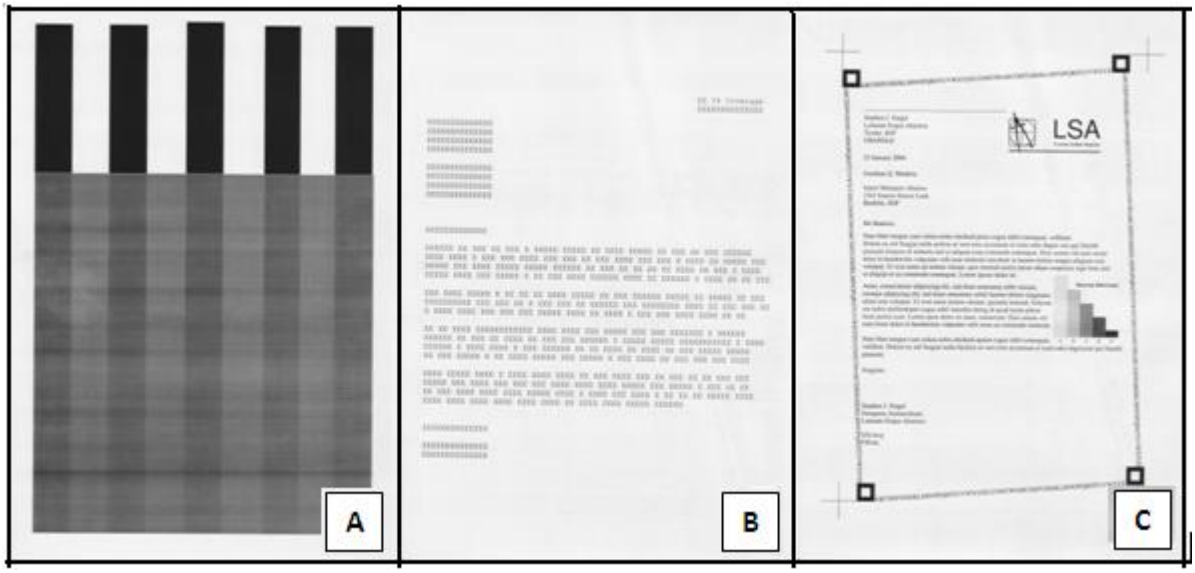


Figure 3.19: Example of test images template (A: thermal banding target, B & C: monochrome toner yield)

Three test prints of M09-FT, M10-FT and M11-FT show a background defects (toner is developed in unprinted areas), leading to grey color of background area. This visual observation is supported by high background density value measured by densitometer (refer Table 3.8). Suda Kiatkamjornwong et al explained that this is probable the result from poor distribution of CCA.[14]

3.5 Comparison between the synthesized toner resin and commercial toner resins

The comparison of properties between sample M10-TR and commercial toner resins is shown in Table 3.13. All of the resins above are styrene acrylic type produced by suspension polymerization. T_g of M10-TR and others commercial toner resins were closed to each other, in the range of 61-63^oC (refer Figure 3.20). Extrapolation of T_g refer to Appendix C (Figure C.19, C.22-C.25).

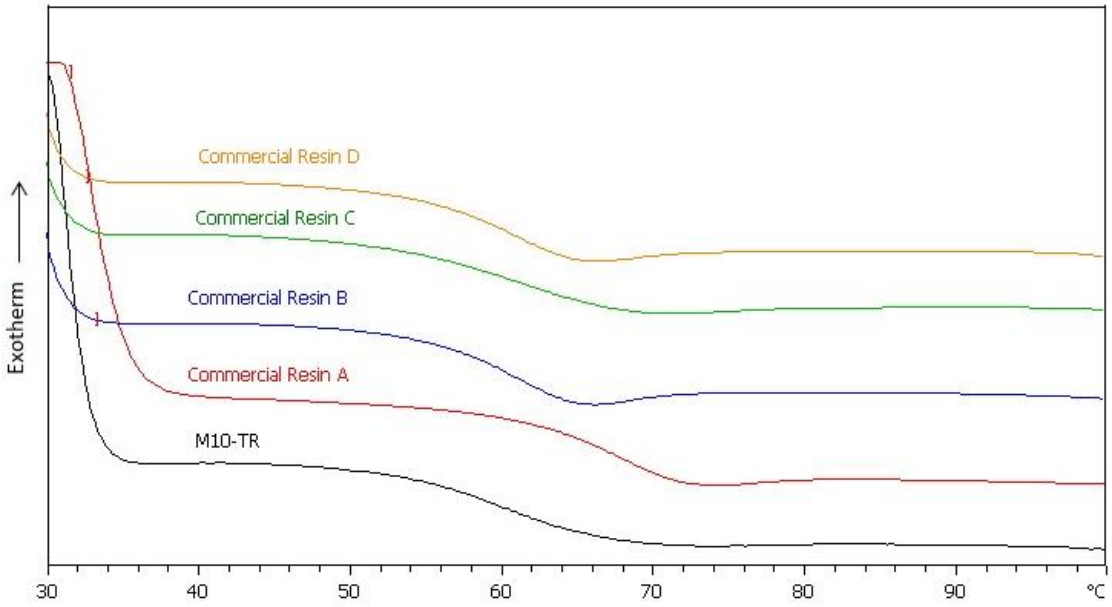


Figure 3.20: DSC thermogram of M10-TR, commercial resin A, commercial resin B, commercial resin C and commercial resin D at the heating rate of 10^oC/min

As for the molecular weight distribution, M10-TR, resin A and resin B have broad and bimodal distribution. The molecular weight distribution of M10-TR measured by the GPC was for the soluble fraction in THF. The gel fraction (insoluble in THF) could not be measured by the GPC. For resin C and resin D, the molecular weight distribution is mono-modal distribution.

M10-TR, resin C and resin D could not fully dissolve in THF. M10-TR contains 9.4% gel content while for resin C is 77% and 54% for resin D. Resin C and resin D contain extra high gel content, which made the molecular weight distribution measured by GPC representing small fraction of soluble part only.

Resin A has the lowest MFI value, with the highest viscosity compared to M10-TR and resin B. Resin B has higher MFI, as its low molecular weight fraction is higher than M10-TR and resin A. Both resin C and resin D could not flow at 150^{o}C. It can be assumed that resin C and resin D have lower MFI value and higher molecular weight than M10-TR, toner A and toner B.

Acid numbers of toner A and toner B were close to each other, around 9.0 mg KOH/g. From the literature, acid number was preferably in the range from 5-50 mg KOH/g to control charging and improve fixability.[65] Acid number of M10-TR, toner A and toner B fulfill the requirement. Acid numbers for toner C and D are too low as these values only represent the soluble fraction in THF.

Table 3.13: Properties of the synthesized toner resin and commercial toner resins

Sample Code	**M10-TR**		**Commercial Resin A**		**Commercial Resin B**		**Commercial Resin C**	**Commercial Resin D**
T_g/ ^oC	61		63		61		63	61
Molecular Weight	**High**	**Low**	**High**	**Low**	**High**	**Low**		
M_n/ x10^3 Daltons	101.37	7.35	159.00	3.54	353.00	8.92	15.00	20.00
M_w/ x10^3 Daltons	316.16	15.01	625.00	5.95	642.00	18.60	39.00	86.00
M_p/ x10^3 Daltons	61.50	18.81	1074.00	4.76	905.00	11.93	20.00	25.00
M_z/ x10^3 Daltons	1107.99	21.17	1521.00	9.08	1151.00	31.68	84.00	371.00
M_w/M_n	3.12	2.04	3.92	1.68	1.82	2.08	2.59	3.58
GPC Peak ratio	59.48	40.52	36.20	63.80	19.91	80.09	-	-
MFI/ g/10min (150^oC)	29.64		4.37		34.16		Can't flow	Can't flow
Acid Number /mg $KOHg^{-1}$	3.02		9.98		9.89		0.50	0.78
%THF Insoluble Fraction	9.38		-		-		77.08	53.77

Chapter 4: Conclusion

4.1 Summary

Styrene acrylic copolymers with the required properties for application as toner resins were prepared by suspension polymerization. The experiments were carried out by varying the monomer ratio, concentration of initiator, and concentration of cross-linking agent. As the styrene content was increased, the T_g of resin has also increased. Higher concentrations of initiator shift the molecular weight distribution to the lower region. Addition of cross-inking agent leads to gel formation. The amount of gel increases rapidly as the amount of cross-linking agent increases from 0.1 to 0.3 parts per 100 parts by weight of total monomers.

High molecular weight and low molecular weight resins were prepared separately and have been mixed at different ratios to obtain broad and bimodal molecular weight distribution. Higher ratio of high molecular weight resins increase the T_g and acid number but lowers the melt flow index. Three samples have been selected to continue for the pilot plant process to produce toner.

The three toners have the properties close to each other in terms of tribocharge, particle size distribution, magnetic content, flowability and apparent density. T_g is in the increasing trend for M09-FT to M11-FT, due to the higher ratio of high MW resin in the toner formulation. MFI value is in the reverse trend. M10-FT toners produce the best print quality as compared to others. Printing tests show minor background defects for samples M09-FT, M10-FT and M11-FT.

Comparison of the synthesized resins and commercial resins has been carried out. All five resins have T_g close to each other. M10-TR, toner A and toner B show bimodal

molecular weight distribution with different peak ratios between the high molecular weight and low molecular weight fractions. Molecular weight distributions of Toners C and D are very broad but mono-modal. This is due to high amount of gel fraction, which could not be measured by GPC. Commercial resins have higher values of acid number than synthesized resin.

All the properties for toner prepared by using resin M10-TR are similar with the properties of toner prepared by using commercial resin A. M10-FT and toner A give the same print quality.

4.2 Presentations at Conferences/Seminars

Parts of the findings have been presented at the following conferences/seminars:

a) Tang, B. K., Gan, S. N., and Rosiyah Y., 2009, Preparation of Styrene Acrylic Copolymers For Toner Resins By Suspension Polymerization, Malaysia Polymer International Conference (MPIC 2009), 21-22 October, Palm Garden Hotel IOI Resort, Putrajaya.

b) Tang, B. K., Gan, S. N., and Rosiyah Y., 2010, The Effect of Different Properties of Toner Resins synthesized by Suspension Polymerization on Image Qualities, 16th Malaysian Chemical Congress (16MCC), 12-14 October, Putra World Trade Centre, Kuala Lumpur.

This project is sponsored by JADI Imaging Technologies Sdn Bhd. The findings are of commercial values, and the Company would like to keep the information as trade secret, and consequently is not in favor of publishing the complete data in journal.

4.3 Suggestion of Future Works

a) Instead of preparing the high and low molecular weight resins separately, the experiment can also be carried out to prepare resin sample which contain both high molecular weight fractions and low molecular weight fractions in a single polymerization system.

b) Suspension polymerization can be used to produce chemically prepared toner.